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Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution

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Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution

NSRDS-NBS no 69

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Radiation Chemistry Data Center
Radiation Laboratory
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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary
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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

E. Ambler.

Ernest Ambler, *Director*

Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution

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Optical absorption spectra are presented for 77 nonmetallic, inorganic radicals and radical ions, produced by radiolysis or photolysis in aqueous solution. This atlas results from the compilation, evaluation, and replotting of spectra from the literature. Additional information is included such as extinction coefficients, initial chemical conditions, methods of transient generation and spectral acquisition, references, mechanisms of transient formation, and notes on dosimetry.

Key words: Absorption spectra; aqueous solution; extinction coefficients; inorganic; radical ions; radicals; transients.

Introduction

Simple inorganic radicals and radical ions in solution have been one of the favorite topics for study in radiation chemistry since the introduction of pulse radiolysis in the early 60's. Some of these radicals had been studied earlier by flash photolysis, but the number of flash photolysis studies increased in parallel with the radiolysis studies. The peak of the research activity on the simple inorganic species came in the late 60's and early 70's. Although many interesting problems remain in this field, a consensus seems to have been reached concerning the identity of the chemical composition of many of these inorganic transients. Such transients are currently being used to form more complicated species in organic and biological systems through oxidation and reduction.

One of the most fruitful techniques that has been used to study the chemistry of the simple inorganic species has been optical absorption spectroscopy. Most of these species absorb ultraviolet and visible radiation. Although optical spectroscopy is not very helpful in determining the exact structure of transients, it is very valuable in following the progress of reactions taking place on the nanosecond or microsecond time scale. Because of this use as a tool to study the kinetics and the use of transient spectra to identify reaction intermediates and individual steps in reaction mechanisms, the optical spectra have become useful data to the experimenter. Since many spectra are now scattered through the literature and since many of these are well characterized, it now seems like an opportune time to collect all of these spectra together in one volume.

It is the purpose of this volume to collect as many spectra of nonmetallic inorganic transients in aqueous solution as possible. The main emphasis has been to collect the most complete and well-characterized spectra that are available in the literature. In addition, special effort was made to obtain extinction coefficients for these spectra.

Explanation of Display and Definition of Symbols and Units

The spectra are displayed on a uniform grid, with a standard 0 to 100 relative absorbance scale and with a standard 500 nm long wavelength scale (1000 nm scale is used for hydrated electron spectrum). The relative absorbance, A, is defined by

$$A = N \times \log_{10} (I_0/I) \qquad (1)$$

In this equation I_0 is the incident intensity of the monitoring light beam at the wavelength being monitored, I is the intensity of the monitoring light beam, at the same wavelength, that is transmitted through the sample, and N is a normalization factor chosen so that the largest absorbance is 100. The wavelengths are given in nanometers (nm) $= 10^{-9}$ meters. An alternative abscissa scale is used in these spectra on the top line of the plots in a scale that is proportional to energy. The units used are cm^{-1}. One eV is approximately 8068 cm^{-1}. To the right of the spectral plots is a sliding extinction coefficient scale.

$$\epsilon = (L[X])^{-1} \log_{10} (I_0/I) \qquad (2)$$

I_0 and I are defined the same as above, L is the length of the optical path, and [X] is the concentration of the absorbing species, X.

In addition to the spectral display, additional information is given. Under the heading "Transient," the transient species is identified; other information which may be included under this heading is the wavelength of the maximum absorbance, an extinction coefficient, and a second-order decay constant, k, defined by

$$d[X]/dt = 2k[X]^2. \qquad (3)$$

The wavelength of the absorption maximum and the extinction coefficient are given under this heading only when explicitly quoted by the experimenters or when taken from another reference. If λ(max) and ϵ are quoted by the experimenters, then the smoothed curves are normalized (see below) to these numbers, both with respect to the ordinate and the abscissa. Extinction coefficients are given in $L\ mol^{-1}\ cm^{-1}$ ($dm^3\ mol^{-1}\ cm^{-1}$); decay rate constants are given in $L\ mol^{-1}\ s^{-1}$ ($dm^3\ mol^{-1}\cdot s^{-1}$). No systematic attempt was made to include the second-order decay rate constants.

The information following the heading "System" concerns the chemical composition of the starting system. Under the headings of "Transient generation" and "Spectral acquisition" the physical equipment used to create the transients and detect them are given. Of particular interest in these two sections is the nature of the dosimetry (measurement of the amount of radiation absorbed in the sample) and actinometry plus the precautions taken to eliminate artifacts, like scattered light. The heading "Reference" contains the literature source of the displayed spectrum.

The information contained under the heading "Transient formation" is of particular interest when transients are prepared in a pulse radiolysis experiment. As opposed to near-ultraviolet or visible photolysis of aqueous solutions where the solutes form the transients in a relatively direct fashion, radiolysis experiments involve the decomposition of the water as a first step. The three major radicals from this process are OH, $e(aq)^-$, and H. The amount of H formed is five or six times less than that of either OH or $e(aq)^-$. These three primary radicals can react with solutes or other transients to form the transients to be studied. Various scavengers are added to prevent the formation of interfering species or to maximize the yield of the transient to be studied. The detailed mechanisms of the authors are given in this section whenever possible, but in many cases these equations are given only as plausible formation equations and should not be understood as precise mechanisms endorsed by the authors who measured the spectrum.

The "Footnotes" are designed mainly to give additional information on alternate extinction coefficients, assumptions on G values,

$$G(X) = \text{number of X radicals formed for 100 eV of the radiation absorbed by the system} \qquad (4)$$

and additional information on special purifications and other precautions.

Criterion for Inclusion

The following standards were set for the spectra to be included in this atlas. Attempts were made to include spectra that contain contributions from only one transient species, have chemical or physical proof of the chemical assignment, correct for instrumental effects like scattered light, give extinction coefficients, and contain a sufficient number of data points to indicate the precision of the smooth spectral curve. These criteria could not always be met. However, in cases where the transients were considered to be important, the spectra were included with some documentation indicating appropriate qualifications. One common problem, for example, is the failure to correct for spectral contributions of species resulting from H atom reactions in pulse radiolysis experiments in aqueous solutions. This is often neglected on the basis of the low yield of hydrogen atoms relative to hydroxyl radicals and hydrated electrons. However, this contribution is not always negligible, and a spectrum must be viewed with some caution when this type of omission occurs.

All of the spectra in this atlas are taken from the literature. Since the pioneering works on these inorganic transients are approximately 10 to 20 years old, newer spectra often exist in private collections and in the literature. These later spectra are often better characterized than the original works. This has been due in large part to refinements in techniques and to better understanding of the chemical processes. One improvement in equipment that has resulted in more reliable spectral shapes has been the interfacing of the experiment to computers. This has allowed the use of convenient signal averaging techniques [1]. In addition, the case of data handling with these systems has allowed the experimenter to explore a larger set of wavelengths [2]. Because of these general advances, spectra that have appeared later in the literature than the pioneering works are often chosen for this atlas over the original works.

Even though spectra obtained from private collections often have these same advantages, it was decided that they should be excluded from the atlas since so many of them were inaccessible to this Data Center. However, the Radiation Chemistry Data Center is collecting these newer spectra and is storing them in a computer-readable form. Spectra will be updated as the Center is made aware of new measurements. Some spectra from private collections are already on file.

Difficulties with Yields and Extinction Coefficients

There is probably much less variability among the various reported spectra of a given transient than among the various reported extinction coefficients of that transient. Many factors could contribute to this difficulty. Among the possible causes are nonuniform irradiation of sample, poor wavelength calibration, faulty dosimetry, scattered light problems, and poor time resolution. Discussion of these and other experimental problems has been thoroughly covered elsewhere [3,4]. However, even when the normal experimental precautions are taken, there remain difficulties. The ultimate source of the problem with extinction coefficients lies in the difficulty of knowing the concentration of a short-lived transient (see eq (2)). Since most of the extinction coefficients in this work are taken from radiolysis works, this means that it is crucial to know the yields (or *G* values) of the primary radicals, the mechanism of production of the transients from these radicals, and the dose of radiation absorbed by the sample in order to calculate the concentration of the species of interest.

The problem of knowing the *G* value is particularly acute, for both the sample itself and for the dosimetry. Usually $G(X)$, itself, is not measured directly. It is usually based on a yield of primary radicals that has been estimated from measured yields at infinite dilution of all scavengers. These yields represent the number of primary radicals that diffuse out of the tracks formed by the ionizing radiation and their secondary electrons. Immediately after the arrival of the high energy radiation, the tracks contain a high density of radicals and other fragments, and many of the radicals combine with each other. Thus only a fraction of the original primary radicals escape into the bulk solution and are measured.

In a usual radiolysis experiment in which absorption spectra are to be measured, scavengers and/or solutes must be added at some finite concentration to react with the primary radicals. However, as the concentration of the scavenger is raised, the chance that the scavenger molecule will initially be present in the volume of a track increases. If this eventually takes place, the primary radicals which would normally combine with other primary radicals in the track will react with the scavenger instead. Thus at high scavenger concentration, scavenging in the track increases the effective yield of primary radicals. The increase in yield depends not only on the scavenger or solute concentration but on the rate constant of the reaction of the scavenger or solute with the primary radicals. This problem has been treated for hydrated electrons [5] and has recently been addressed for hydroxyl radicals [6].

Extinction coefficients can be corrected for scavenging of primary radicals in tracks if the scavenger concentration is known, if the rate constant of the scavenging reaction is known, and if a calibration curve is available. Some calibration curves do now exist [5], but not enough supplementary information is available to make corrections for many cases in the literature. For example, since dosimetry usually involves measuring some well-known transient, it is necessary to know concentrations in the dosimeter as well as in the sample under study. Since corrections cannot be made in many cases, none of the extinction coefficients reported within have these corrections. However, much of the supplementary information that would be needed to make these corrections is included.

Digitization Methods and Their Sources of Errors

The transcription of the spectra from the literature to the standard format reported in this atlas has led to some unavoidable errors in the resulting data. In order to document the errors, a brief description of the transcription procedure and the possible errors in each step are presented for reference. The data were taken from the literature by first photocopying and then digitizing the spectra from the photocopy. If the drawing was too small for accurate digitization, the photocopy was enlarged before the spectrum was digitized. Where possible the spectra were digitized directly from reprints of journal articles. The digitizer consisted of a digital voltmeter connected to the slide wires of an X–Y recorder. A seven-power comparator was attached to the slide wires to improve both accuracy and precision of each reading.

---

[1] Figures in brackets indicate literature references at the end of the text.

For normal-sized, full-column graphs taken from an American Chemical Society journal with the ordinate ranging from 0 to 100 and the abscissa covering a 200 nm range, the reproducibility of the digitizer was ±0.5% for the ordinate and ±1 nm for the abscissa. Most of the curves reproduced will have similar uncertainties in the ordinate from the digitization process itself. However, the uncertainties in the abscissa will vary since the wavelength range of the original figures cover a wide range. When the original drawing has the full 500 nm range, the uncertainty in the abscissa might be as large as ±3 nm.

In general, the ultimate accuracy is probably not limited by the reproducibility of the digitizer. Other sources of error enter between the data from the author and the final reproduction. One source of distortions is the optics of the xerography and enlarging processes. Some pincushion distortions were found, particularly in the xerography process. In some cases it was found that figures in the literature had their own inherent distortions that had entered in the processing of the initial raw data to the final journal spectrum. Thus a loss in accuracy due to these processes is very difficult to estimate. However, in the overall reproduction process from the literature, it is estimated that the data presented here are accurate to better than ±2% of the maximum extinction coefficient. The spectral plots were made with a Versatec electrostatic plotter. The resolution of the plots is 200 dots per inch.

All of the continuous spectral curves, but not the data points themselves, that were digitized from the literature were put through a smoothing procedure involving a fast Fourier transform [7]. This procedure had the advantage of averaging the digitization of the spectral curves from the literature, which have the best likelihood of representing the shape of the spectra. Intermediate steps in the smoothing process were displayed on a video GT 62 terminal made by the Digital Equipment Corporation. The output from the smoothing routine is a set of extinction coefficients at regular wavelength intervals. This output was stored in permanent computer files and was plotted along with the individual, digitized data points to give the displayed spectra in this volume. When an ϵ(max) was quoted by the authors, the ordinate and abscissa of the plots containing the digitized data were checked and adjusted to match the quoted values.

Acknowledgements

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Symbols and Abbreviations

A	absorbance (optical density)
ϵ	extinction coefficient (molar absorption coefficient)
G	radiation yield (molecules per 100 eV)
k	rate constant
krad	dose absorbed (6.24×10^{16} eV per g) = 10 Gy
K	equilibrium constant
λ	wavelength (nm)
pK_a	$-\log_{10}$ dissociation constant
PMT	photomultiplier tube

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[1] Patterson, L. K., and Lilie, J., Int. J. Radiat. Phys. Chem. **6**(2), 129-41 (1974).

[2] Gordon, S., Schmidt, K. H., and Martin, J. E., Rev. Sci. Instr. **45**(4), 552-8 (1974).

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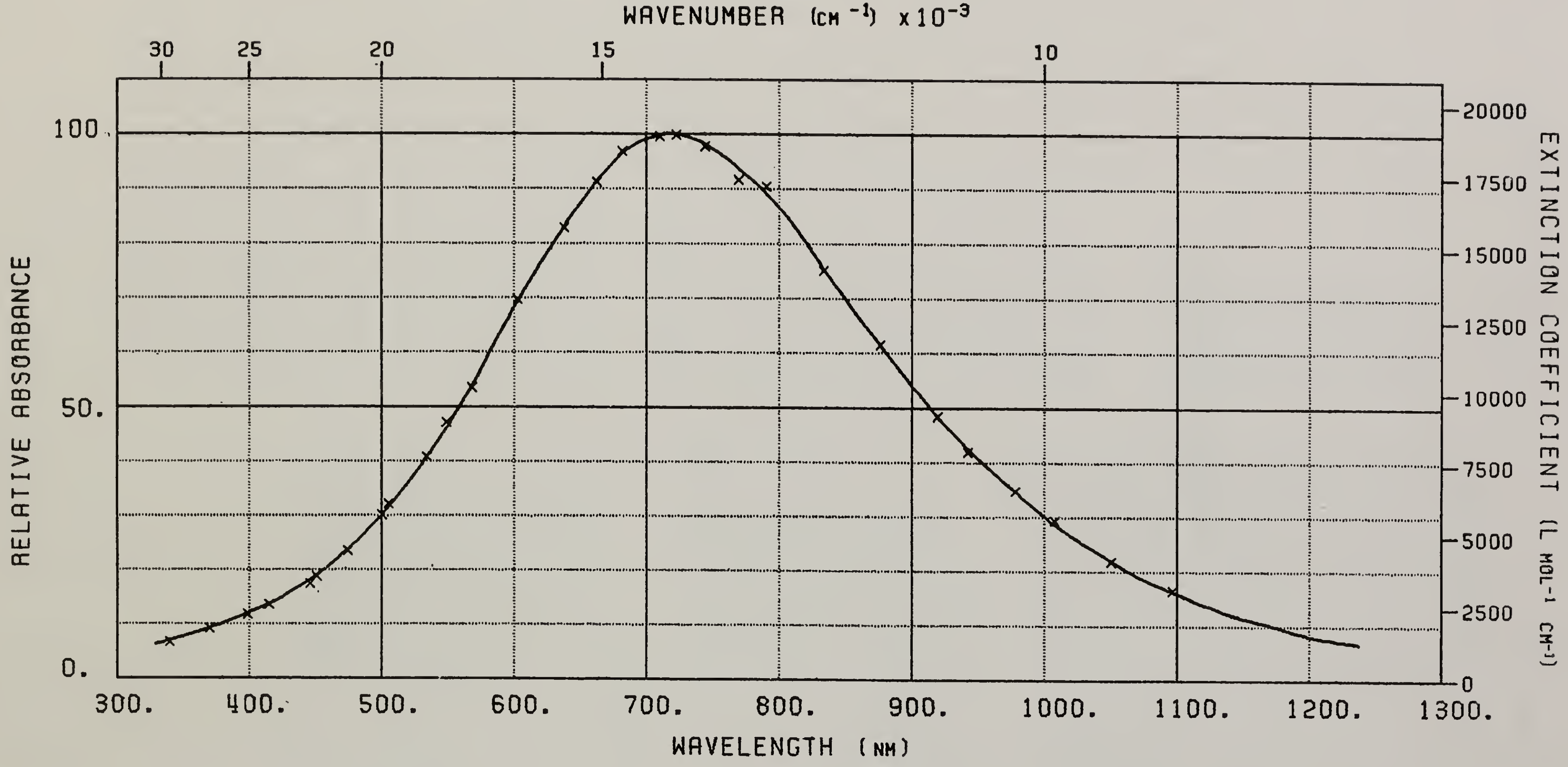
[5] Balkas, T. I., Fendler, J. F., and Schuler, R. H., J. Phys. Chem. **74**, 4497-505 (1970).

[6] Schuler, R. H., Patterson, L. K., and Janata, E., J. Phys. Chem. **84**(16), 2088-9 (1980).

[7] Helman, W. P., unpublished work, 1979.

Spectra of Transients

$e(aq)^-$



Transients: $e(aq)^-$, hydrated electron, λ(max) = 720 nm, ϵ_{720} = 1.9 x 10^4 L mol^{-1} cm^{-1} [1]

System: water (triply distilled), 300 K, 1 bar

$e(aq)^-$

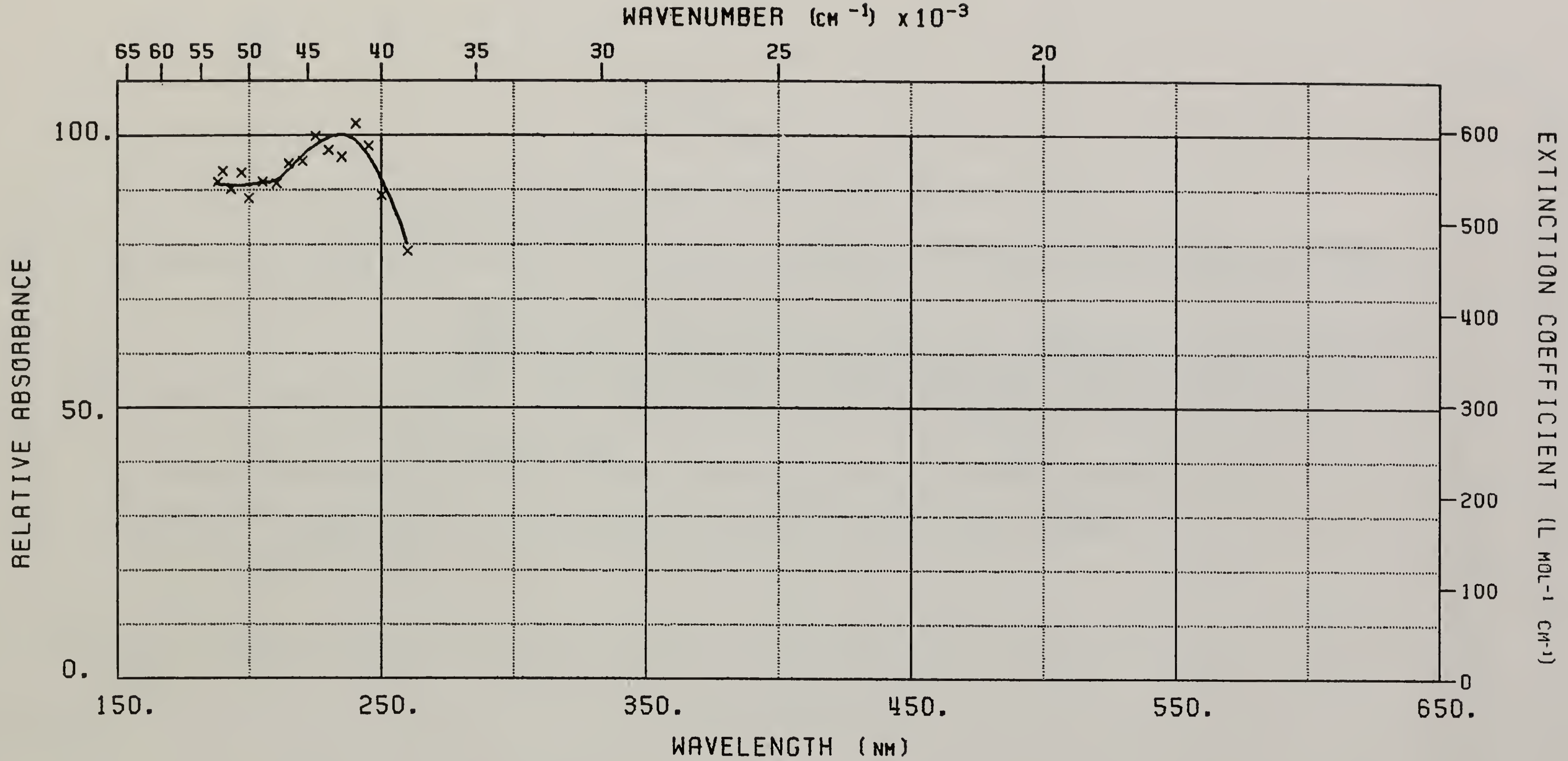
Reference: F.-Y. Jou and G.R. Freeman, J. Phys. Chem. 81(9): 909-15 (1977)

Transient generation: 2.1 MeV electrons; pulse width 1.0 μs; dosimetry KSCN [2]; steel pressure cell

Spectral acquisition: In UV range: Bausch 8 Lomb 33-86-07 grating in monochromator, band pass = 7 nm; RCA 1P28 PMT; Corning filter were used to eliminate higher order light interference. In visible and ir region [3] gratings were 33-86-02, -03, and -78; infrared photocell, Barnes Engineering A-10D/D10S InSb diode cooled to 77 K.

Footnotes:
[1] G.L. Bolton, K.N. Jha, and G.R. Freeman, Can. J. Chem., 54(10): 1497-506 (1976).
[2] Dosimetry oxygen saturated 5×10^{-3} mol L^{-1} KSCN using $G\epsilon_{478}((SCN)_2^-) = 21000$ $(100 \text{ eV mol } L^{-1} \text{ cm})^{-1}$.
[3] F.-Y. Jou and G.R. Freeman, Can. J. Chem. 54(23): 3693-704 (1976).

OH



Transient [1]: OH, hydroxyl radical, ϵ_{188} = 540 L mol^{-1} cm^{-1} [2]

System: aqueous solution of 5.25 x 10^{-5} mol L^{-1} NaOH and 5.0 x 10^{-4} mol L^{-1} N_2O, T = 302 K

OH

Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, J. Phys. Chem. 80(22): 2482-8 (1976)

Transient generation: pulse radiolysis using 0.5 μs pulses of 7 MeV electrons; dose per pulse 6.6 krad [3]; dose variations monitored by charge collection method [4]

Spectral acquisition: two Bausch & Lomb high-intensity grating monochromators connected in series [5]; bandwidth at half-max intensity = 4.8 nm; light path purged with N_2 [6]; solar-blind PMT (R166, H.T.V. Co., Japan) [7]; XBO 450 W/4 xenon lamp (Osram) with Suprasil envelope operated with a transitorized pulser which intensifies lamp by 30-fold; time delay 0.8 μs after pulse

Transient formation:

OH formed in primary processes of radiolysis of H_2O also

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$$

Footnotes:

[1] The long wavelength portion of the spectrum is thought to be a $^2\Pi \rightarrow {}^2\Sigma^+$ transition that is perturbed by H-bonding to H_2O. At wavelengths shorter than 200 nm, the authors think that the intensity may be from a transition in H_2O that is perturbed by the presence of an OH radical. There is an alternate explanation of the spectrum in the literature.

[2] Absorbances were corrected for OH^-, H_2O_2, and N_2O. Reactions of these species and the transients were simulated by a computer program using available rate constants. Rate of $2k(H+H) = 1.55 \times 10^{10}$ L mol^{-1} s^{-1} and $G(e(aq)^-) = 2.80$; $G(H^+) = 2.90$; $G(OH) = 2.70$; $G(OH^-) = 0.10$; $G(H) = 0.48$; $G(H_2) = 0.45$; $G(H_2O_2) = 0.70$; $G(HO_2) = 0.02$.

[3] Sample changed after each pulse.

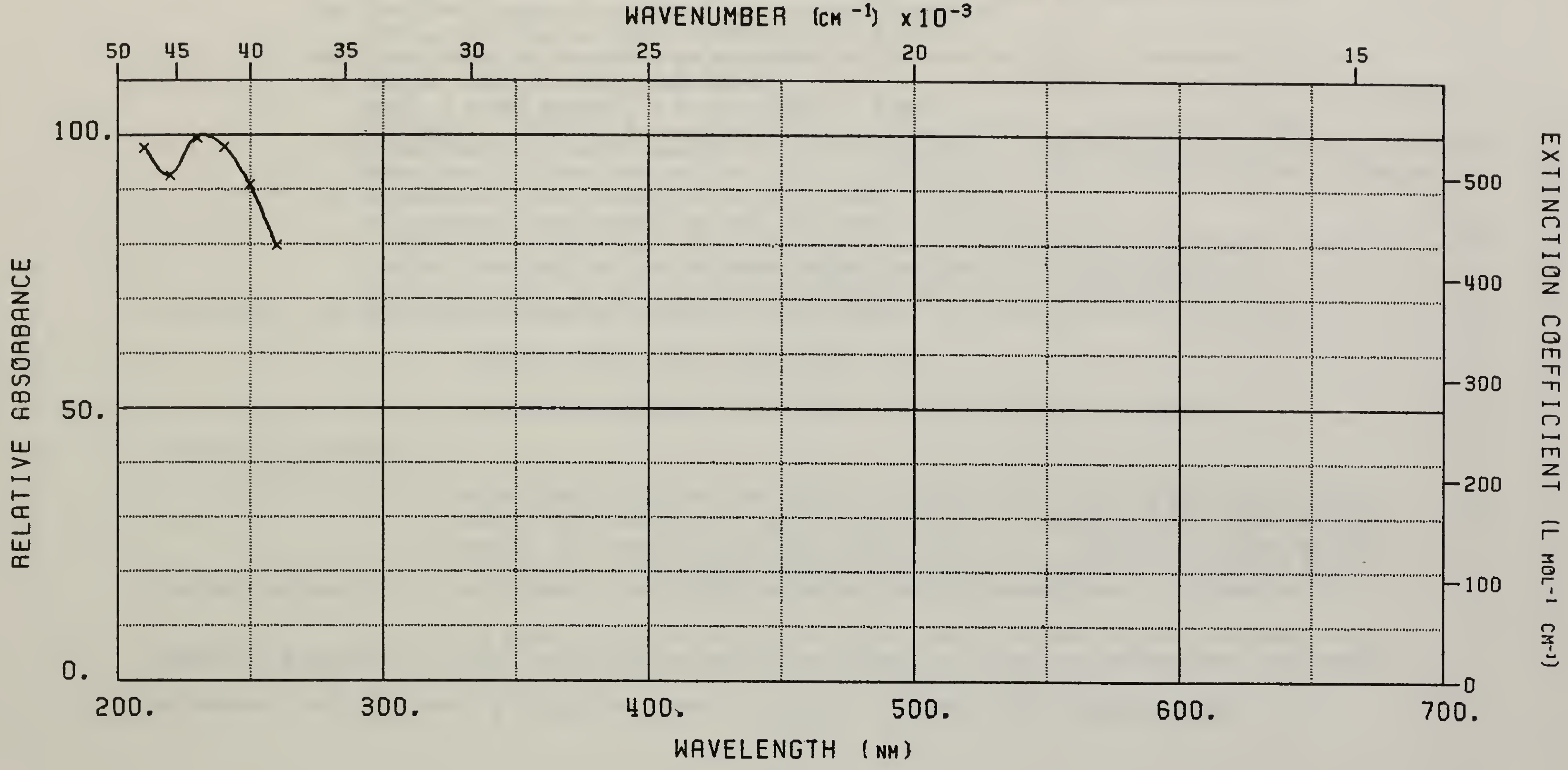
[4] Total dose was obtained by matching the calculated $e(aq)^-$ transient with that observed at 600 nm using alkaline solution.

[5] Gratings blazed for maximum efficiency at 250 nm.

[6] With this system transient spectra could be measured to 182 nm, but H_2O absorption interfered below 188 nm.

[7] Amount of scattered light at the shortest wavelength was less than 1%.

OD



Transient [1,2]: OD

System: D_2O solution of 3×10^{-5} mol L^{-1} $DClO_4$ and 2×10^{-3} mol L^{-1} N_2O

OD

Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, J. Phys. Chem. 80(22): 2482-8 (1976)

Transient generation [3]: pulse radiolysis; pulse energy 10-11 MeV; pulse length 1.0 μs; dosimetry $K_4Fe(CN)_6$ [4]; dose per pulse ≈ 5 krad

Spectral acquisition [3]: Osram xenon lamp XBO 450 with Suprasil quartz bulb; lamp pulsed resulting in an increase in brightness of 25-30 times the nonpulsed lamp; optical windows of cell were of Suprasil quartz; lenses were of Suprasil quartz; Zeiss MM 12 double quartz prism monochromator [5]; EMI 9558Q PMT [6]; time delay, extrapolated back to zero

Transient formation:

OD from radiolysis of D_2O

$$e(sol)^- + N_2O\ (+D_2O) \rightarrow OD + OD^- + N_2$$

Footnotes:

[1] The long wavelength portion of the spectrum is thought to be a $^2\Pi \rightarrow {}^2\Sigma^+$ transition. At wavelengths shorter than 200 nm, the authors think that the intensity may be from a transition in D_2O that is perturbed by the presence of an OD radical. There is an alternate explanation of the corresponding OH spectrum in the literature.

[2] Calculation of concentrations were made using G(D) = 0.44, $G(e(sol)^-)$ = 2.90, G(OD) = 2.90, $G(D_2O_2)$ = 0.62 with a small correction for radical recombination during pulse.

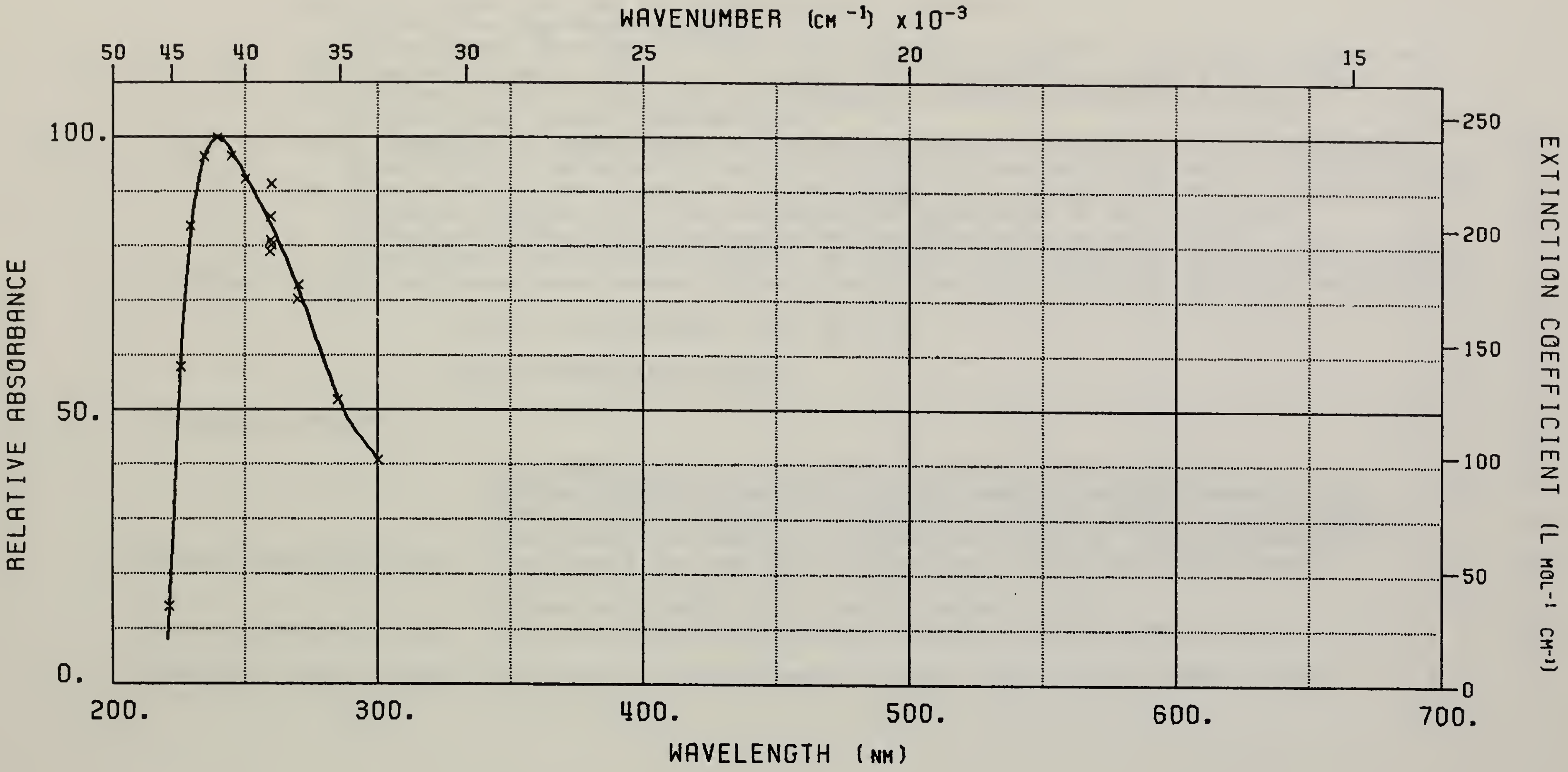
[3] P. Pagsberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S.O. Nielsen, J. Phys. Chem. 73(4): 1029-38 (1969).

[4] Aqueous solution of 10^{-3} mol L^{-1} $K_4Fe(CN)_6$ saturated with N_2O; $G(Fe(CN)_6{}^{3-})$ = $G(OH) + G(e(aq)^-)$ = 2.65 + 2.6 = 5.25 and $\epsilon_{420}(Fe(CN)_6{}^{3-})$ = 1000 L mol^{-1} cm^{-1}.

[5] No scattered light could be detected at 200 nm; at maximum slit width of 2.0 mm the bandwidth at 200 nm was 0.95 nm.

[6] Monochromator and PMT set behind a 10 cm lead shield.

O^-



Transient: O^-, λ(max) = 240 nm, ϵ_{240} = 240 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 0.105 mol L^{-1} NaOH, pH = 13, 0.5 atmospheres N_2O, carbonate free

O^-

Reference: J. Rabani, Advan. Chem. Ser. 81: 131-52 (1968)

Transient generation: pulse radiolysis using syringe technique; electron beam monitored by split beam technique [2]

Spectral acquisition: 450 W Osram xenon monitoring lamp, corrections made for scattered light [3]; Bausch & Lomb monochromators

Transient formation:

$$H + OH^- \rightarrow e(aq)^- \ (+H_2O)$$

$$e(aq)^- + N_2O \ (+H_2O) \rightarrow N_2 + OH^- + OH$$

$$e(aq)^- + N_2O \rightarrow N_2 + O^-$$

$$OH + OH^- \rightleftharpoons O^- + H_2O, \ pK_a(OH) = 11.85$$

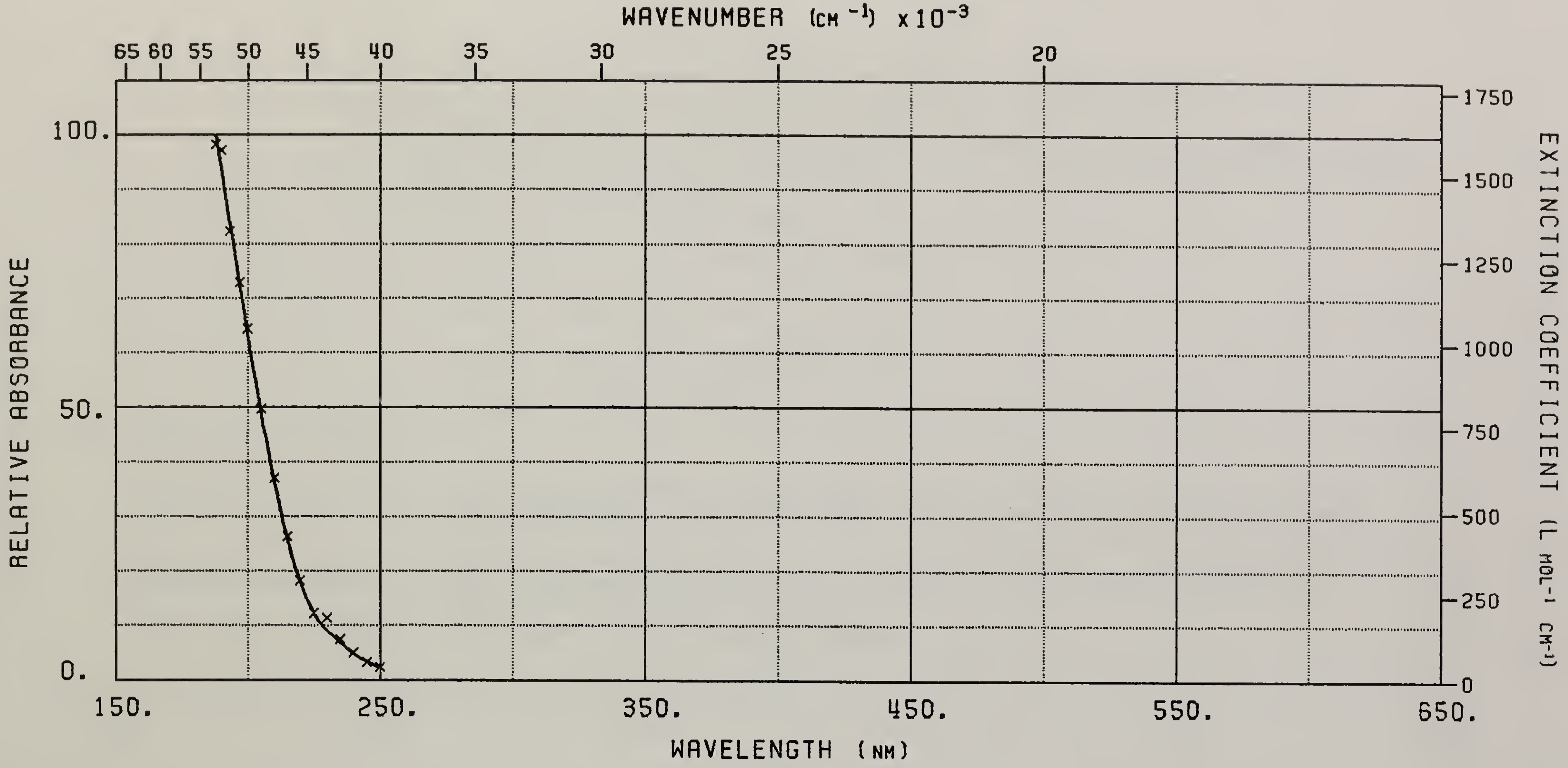
Footnotes:

[1] Using $G(OH) + G(O^-) = 5.8$ and $G(H_2O_2) = 0.7$. Corrections were made for the absorption of OH and H_2O_2.

[2] One beam was passed through a monochromator set at 260 nm to monitor the electron beam intensity. Absolute dosimetry used 5×10^{-4} mol L^{-1} $K_4Fe(CN)_6$ under experimental conditions, taking $\epsilon_{420} = 1000$ L mol^{-1} cm^{-1}.

[3] Depending on the optical alignment, the scattered light was 3-6% at 260 nm, 8% at 250 nm, 10-15% at 240 nm, 20-25% at 230 nm, and 50% at 222 nm.

H in H_2O



Transient [1]: H atom in H_2O, ϵ_{188} = 1620 L mol^{-1} cm^{-1} [2]

System: aqueous solution of 3.39 x 10^{-4} mol L^{-1} $HClO_4$, 2.82 x 10^{-2} mol L^{-1} H_2 (30 atm), and 4.5 x 10^{-5} mol L^{-1} H_2O_2 (steady state concentration from radiolysis), T = 307 K

H in H_2O

Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, J. Phys. Chem. 80(22): 2482-8 (1976)

Transient generation: pulse radiolysis using 1.0 μs pulses of 7 MeV electrons; dose per pulse 3.3 krad; dose variations monitored by charge collection method [3]

Spectral acquisition: two Bausch 8 Lomb high-intensity grating monochromators connected in series [4]; bandwidth at half-max intensity = 4.8 nm; light path purged with N_2 [5]; solar-blind PMT (R166, H.T.V. Co., Jpn) [6]; XBO 450 W/4 xenon lamp (Osram) with Suprasil envelope operated with transistorized pulser which intensifies lamp by 30-fold; time delay 1.0 μs after pulse

Transient formation:

H from primary processes in radiolysis of H_2O

$e(aq)^- + H^+ \rightarrow H$

$OH + H_2 \rightarrow H_2O + H$

Footnotes:

[1] Authors assign the spectrum to a transition that mainly involves the H_2O molecule. The excited state was thought to involve a partial negative charge transfer to a neighboring H atom. The ground state was not perturbed by the H atom. There are alternate assignments of this spectrum in the literature.

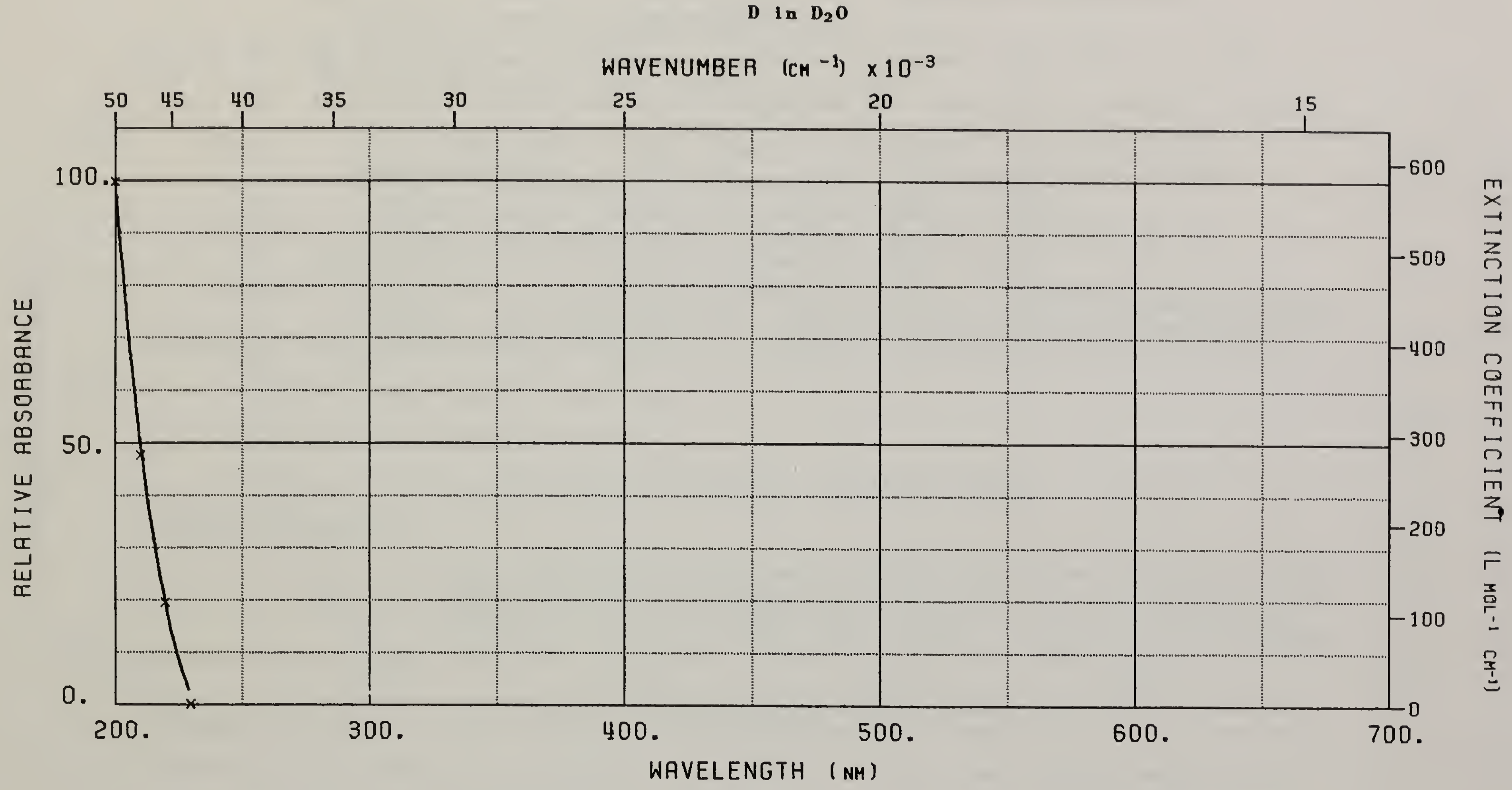
[2] Absorbances were corrected for presence of H_2O_2. This correction was made using the calculated concentrations for H_2O_2 and transient species that were obtained by a computer simulation of the overall reaction using available rate constants. Yields used were $G(e(aq)^-) = 2.80$; $G(H^+) = 2.90$; $G(OH) = 2.70$; $G(OH^-) = 0.10$; $G(H) = 0.48$; $G(H_2) = 0.45$; $G(H_2O_2) = 0.70$; $G(HO_2) = 0.02$. Correction was made for radiation-induced absorption of quartz cell used for high pressures.

[3] Total dose was obtained by matching the calculated $e(aq)^-$ transient with that observed at 600 nm using alkaline solution.

[4] Gratings blazed for maximum efficiency at 250 nm.

[5] With this system transient spectra could be measured to 182 nm, but H_2O absorption interfered below 188 nm.

[6] Amount of scattered light at the shortest wavelength was less than 1%.



Transient [1,2]: D atom in D_2O

System: D_2O solution of 10^{-3} mol L^{-1} $DClO_4$

D in D_2O

Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, J. Phys. Chem. 80(22): 2482-8 (1976)

Transient generation [3]: pulse radiolysis; pulse energy 10-11 MeV; pulse length 1.0 μs; dosimetry $K_4Fe(CN)_6$ [4]; dose per pulse ≈ 5 krad

Spectral acquisition [3]: Osram xenon lamp XBO 450 with Suprasil quartz bulb; lamp pulsed resulting in an increase in brightness of 25-30 times the nonpulsed lamp; optical windows of cell were of Suprasil quartz; lenses were of Suprasil quartz; Zeiss MM 12 double quartz prism monochromator [5]; EMI 9558Q PMT [6]; time delay, extrapolated back to zero

Transient formation:

D from radiolysis of D_2O

$D^+ + e(sol)^- \rightarrow D$

Footnotes:

[1] Authors assign the spectrum to a transition that mainly involves the D_2O molecule. The excited state was thought to involve a partial negative charge transfer to a neighboring D atom. The ground state was not perturbed by the D atom. There are alternate assignments of the corresponding H atom spectrum in the literature.

[2] Calculation of concentrations were made using $G(D) = 0.44$, $G(e(sol)^-) = 2.90$, $G(OD) = 2.90$, $G(D_2O_2) = 0.62$ with a small correction for radical recombination during pulse.

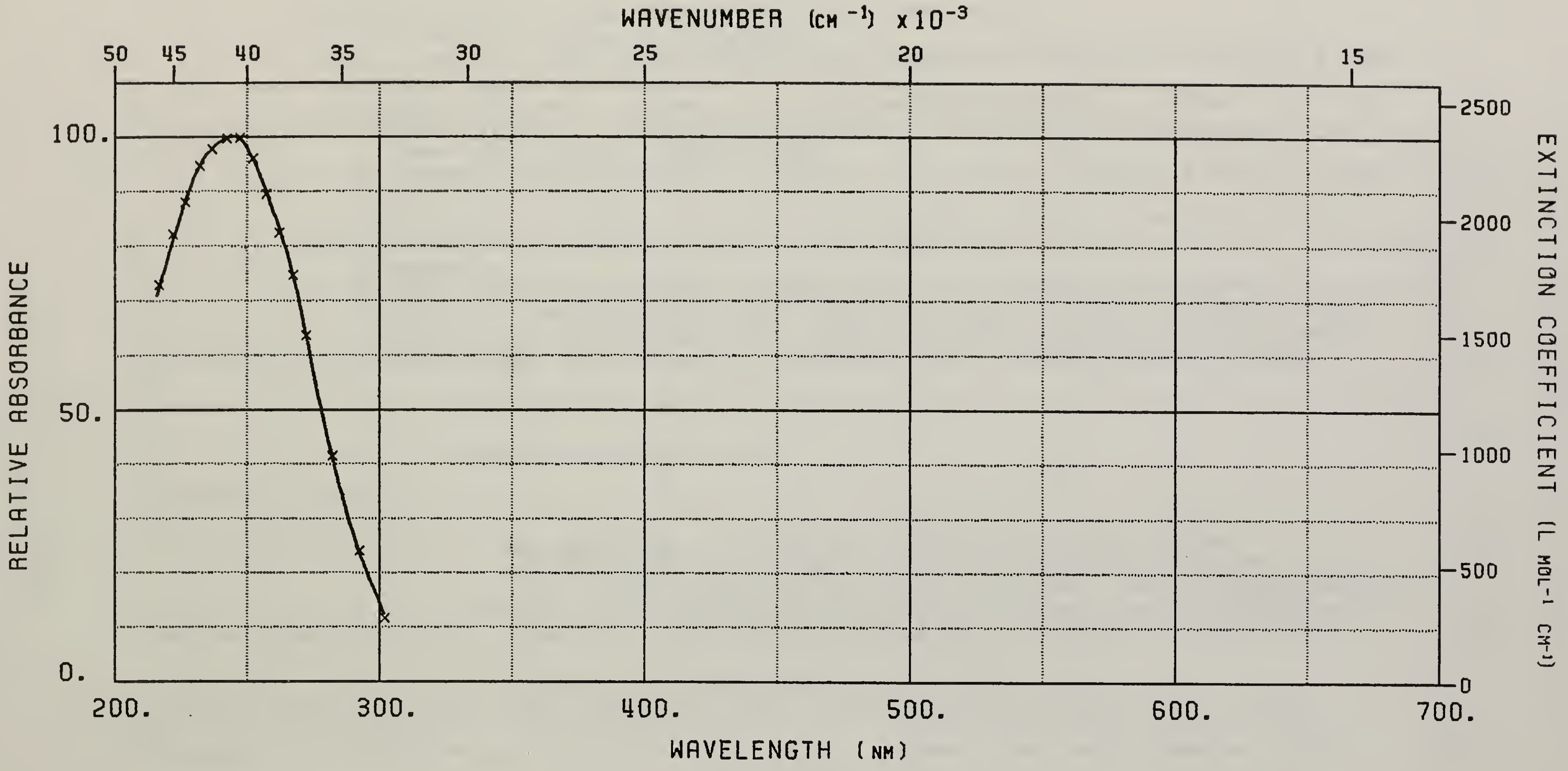
[3] P. Pagsberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S.O. Nielsen, J. Phys. Chem. 73(4): 1029-38 (1969).

[4] Aqueous solution of 10^{-3} mol L^{-1} $K_4Fe(CN)_6$ saturated with N_2O; $G(Fe(CN)_6{}^{3-}) = G(OH) + G(e(aq)^-) = 2.65 + 2.6 = 5.25$ and $\epsilon_{420}(Fe(CN)_6{}^{3-}) = 1000$ L mol^{-1} cm^{-1}.

[5] No scattered light could be detected at 200 nm; at maximum slit width of 2.0 mm, the bandwidth at 200 nm was 0.95 nm.

[6] Monochromator and PMT set behind a 10 cm lead shield.

O_2^-



Transient: O_2^-, superoxide radical ion, λ(max) = 245 nm, ϵ_{245} = (2350   12)) L mol^{-1} cm^{-1} [1,2], k(O_2^- + O_2^-) less than 0.35 L mol^{-1} s^{-1}

System: air-saturated, aqueous [3] 10^{-2} mol L^{-1} sodium formate solution, containing 10^{-4} mol L^{-1} EDTA [4] and Na_3PO_4 [5] added to adjust pH to 10.5

O_2^-

Reference: B.H.J. Bielski, Photochem. Photobiol. 28: 645-9 (1978)

Transient generation: pulse radiolysis, using stopped-flow technique [6]

Spectral acquisition:

Transient formation:

$e(aq)^- + O_2 \rightarrow O_2^-$

$H + O_2 \rightarrow HO_2$

$OH^- + HO_2 \rightleftharpoons O_2^- + H_2O$, $pK_a(HO_2) = 4.69 \pm 0.08$

$OH + HCOO^- \rightarrow CO_2^- + H_2O$, $pK_a(HCOOH) = 3.77$

$CO_2^- + O_2 \rightarrow O_2^- + CO_2$

Footnotes:

[1] Based (a) on extinction coefficient of nitroform radical anion, $C(NO_2)_3^-$, which was formed by the reaction of O_2^- and tetranitromethane and (b) on difference in 550 nm extinction coefficients of ferrocytochrome c and ferricytochrome c. The ferrocytochrome c was formed by the reaction of O_2^- with ferricytochrome c. No $G(O_2^-)$ was assumed with this method.

[2] Earlier values for ε(max) are listed in the review by G. Czapski, Ann. Rev. Phys. Chem. 22: 171-208 (1971).

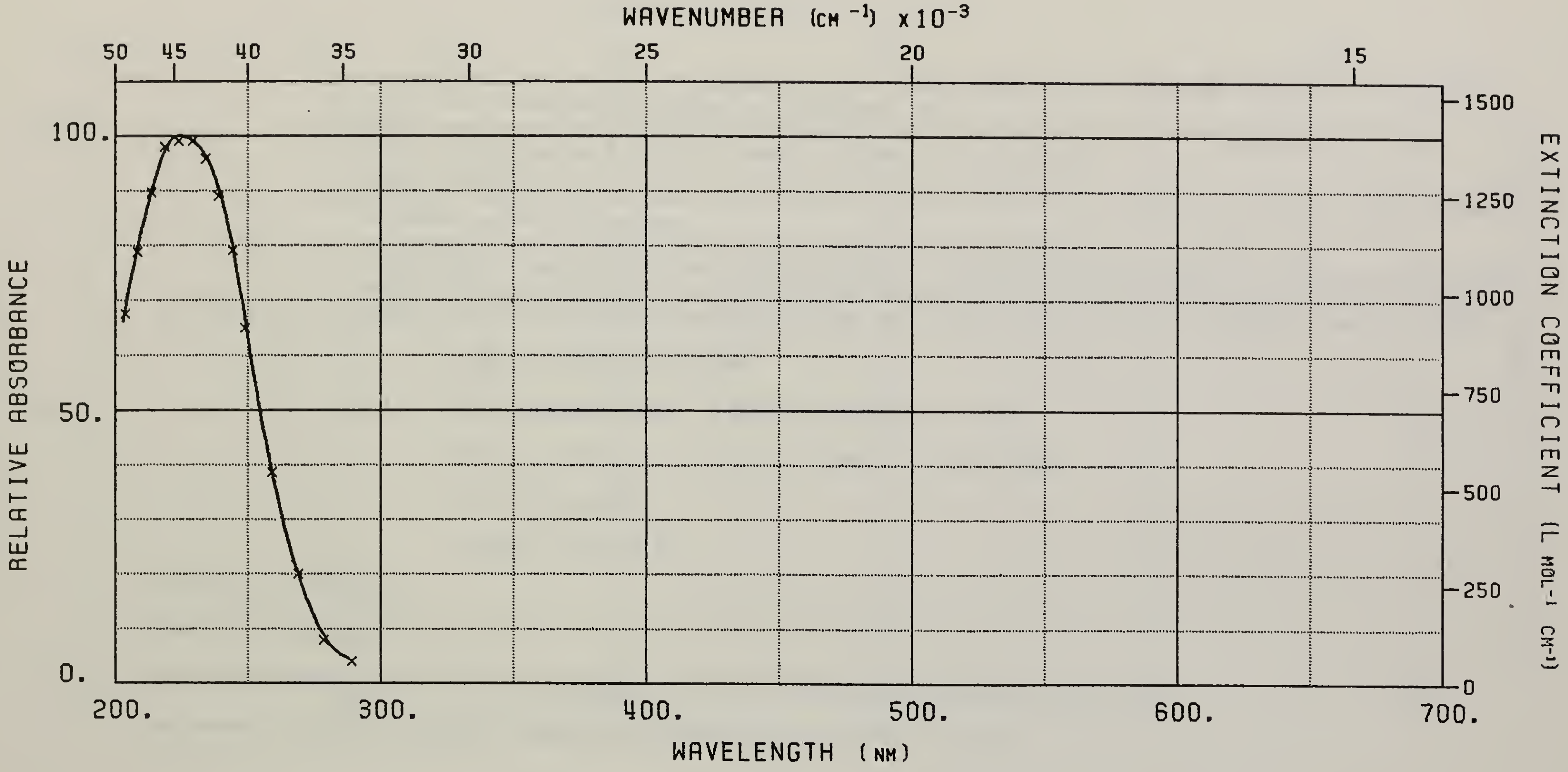
[3] Water purified by a Milli-Q reagent grade water system.

[4] Added to remove heavy metal ions which can catalyze O_2^- disproportionation.

[5] Purified using method given in reference [6].

[6] B.H.J. Bielski and H.W. Richter, J. Am. Chem. Soc. 99(9): 3019-23 (1977).

HO_2



Transient: HO_2, perhydroxyl radical, λ(max) = 225 nm, ϵ_{225} = (1400 ± 80) L mol^{-1} cm^{-1} [1,2], $k(HO_2 + HO_2)$ = (8.60 ± 0.62) x 10^5 L mol^{-1} s^{-1}

System: air-saturated, aqueous [3] 10^{-2} mol L^{-1} sodium formate solution with pH adjusted to 1.5 using perchloric acid

HO_2

Reference: B.H.J. Bielski, Photochem. Photobiol. 28: 645-9 (1978)

Transient generation: pulse radiolysis, using stopped-flow technique [4]

Spectral acquisition:

Transient formation:

$e(aq)^- + H^+ \rightarrow H$

$H + HCOOH \rightarrow CO_2H + H_2$, $pK_a(HCOOH) = 3.77$

$OH + HCOOH \rightarrow CO_2H + H_2O$

$CO_2H + O_2 \rightarrow O_2^- + CO_2 + H^+$

$O_2^- + H^+ \rightleftharpoons HO_2$, $pK_a(HO_2) = 4.69 \pm 0.08$

Footnotes:

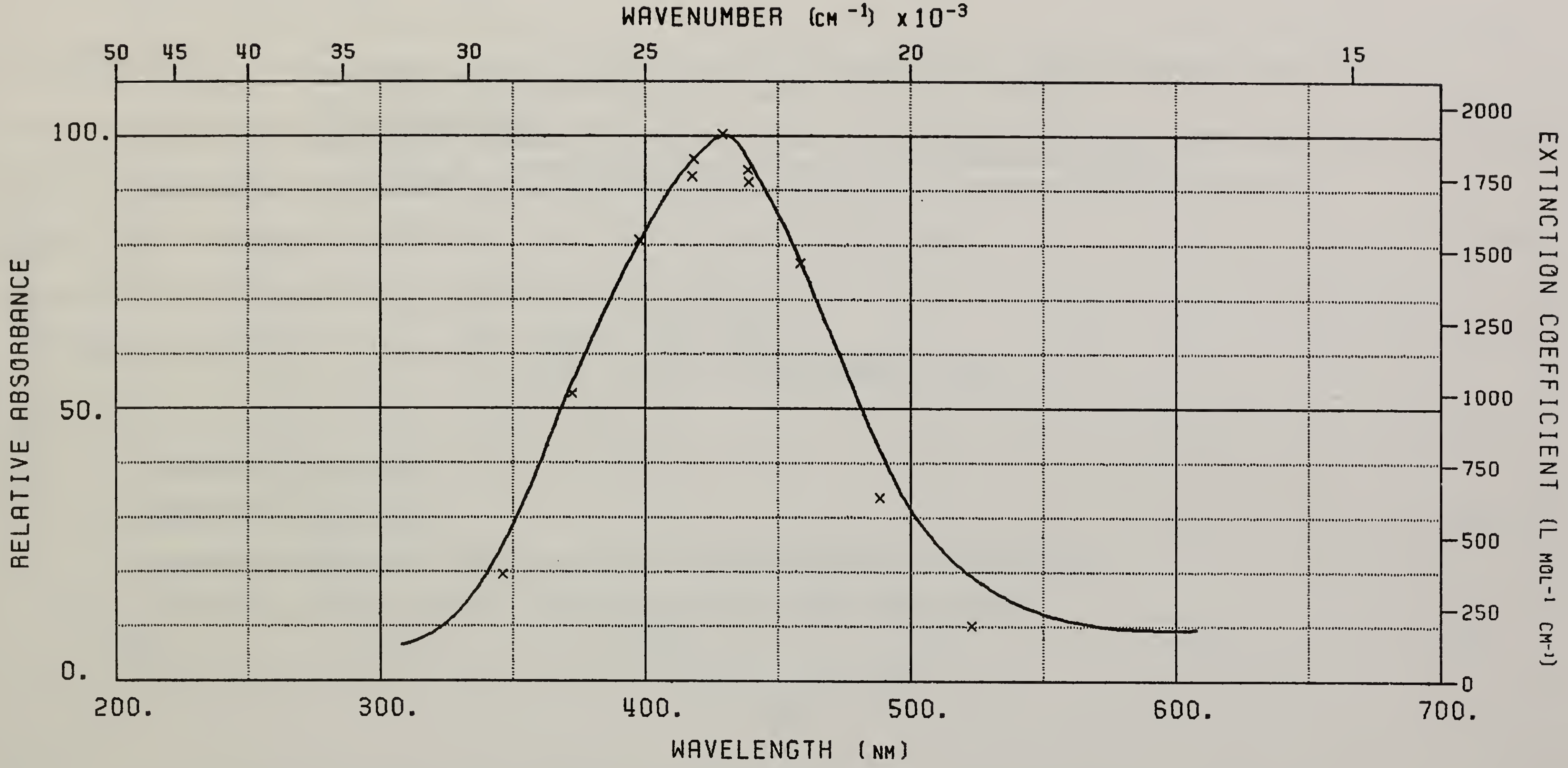
[1] Determined from calibrations of beam current based on O_2^- concentration, where O_2^- concentration was obtained without assuming a $G(O_2^-)$.

[2] Earlier values for $\epsilon(max)$ are given by G. Czapski in Ann. Rev. Phys. Chem. 22: 171-208 (1971).

[3] Water purified by a Milli-Q reagent grade water system.

[4] B.H.J. Bielski and H.W. Richter, J. Am. Chem. Soc. 99(9): 3019-23 (1977).

O_3^-



Transient [1]: O_3^-, ozonide ion, ϵ_{430} = (1900 ± 120) L mol^{-1} cm^{-1} [2]

System: aqueous solution of O_2 and N_2O with $[N_2O]/[O_2] \approx 20$, pH ≈ 13.5 [3]

O_3^-

Reference: W.D. Felix, B.L. Gall, and L.M. Dorfman, J. Phys. Chem. 71(2): 384-92 (1967)

Transient generation: pulse radiolysis using a Varian V-7715A linear accelerator, syringe technique; dosimetry [4]

Spectral acquisition: 500 W Osram xenon lamp (Type XBO 450 W); 1P28 PMT; two Bausch & Lomb grating monochromators (Type 33-86-25, f/3.5) with light beam split by partially reflecting mirror; bandwidth: less than 1.8 nm

Transient formation:

$$e(aq)^- + N_2O \rightarrow N_2 + O^-$$

$$OH^- + OH \rightarrow H_2O + O^-, \ pK_a(OH) = 11.85$$

$$O^- + O_2 \rightarrow O_3^-$$

Footnotes:

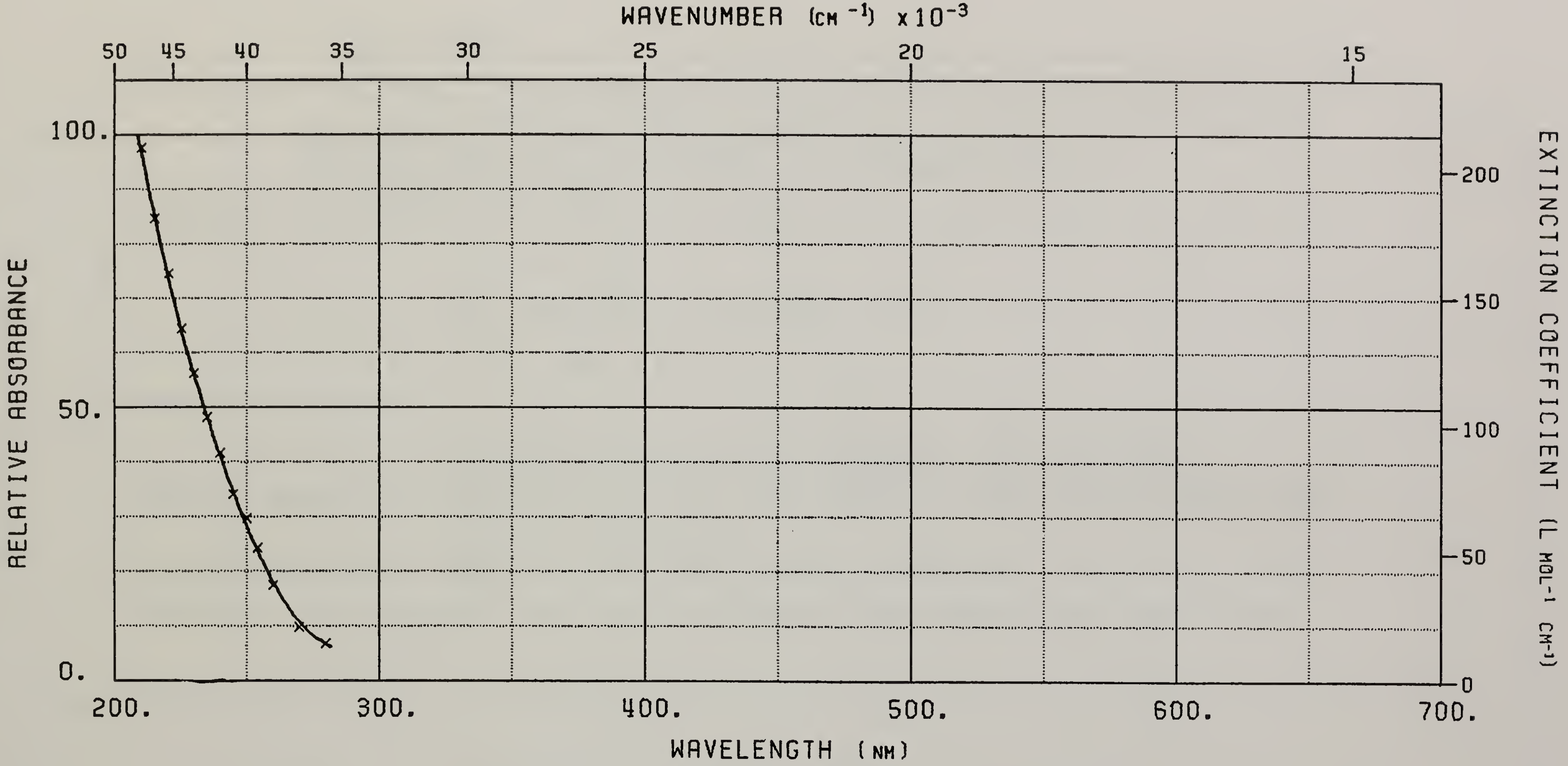
[1] Solid curve is drawn from a composite of the data presented plus data from a solution free of N_2O.

[2] Based on $G(O^-) = 3.3$ at $pH = 13.1$ in O_2-saturated solution.

[3] Under these conditions most $e(aq)^-$ are converted to O^-.

[4] Dosimeter was an O_2-saturated sulfuric acid solution with no chloride ions and with 10^{-2} mol L^{-1} Fe^{2+}. At high dose rates, $G(Fe^{3+}) = 15.6$. At low dose, $\epsilon_{304}(Fe^{3+}) = 2200$ L mol^{-1} cm^{-1} was used to calculate dose. At high intensity, dose was calculated by monitoring 366 nm and by using $\epsilon_{304}/\epsilon_{366} = 8.9$ for Fe^{3+}.

H_2O_3



Transient: H_2O_3, hydrogen sesquioxide [1]

System: air-saturated, aqueous 10^{-2} mol L^{-1} $HClO_4$, pH ≈ 2

H_2O_3

Reference: B.H.J. Bielski and H.A. Schwarz, J. Phys. Chem. 72(11): 3836-41 (1968)

Transient generation: electrons from 2 MeV Van de Graaff generator; variable pulse length, a few hundred microseconds to several tenths of a second; ferrous dosimetry

Spectral acquisition: deuterium analyzing lamp; optical path length = 6.1 cm; Bausch & Lomb f/3.5 monochromator; tandem monochromators used below 240 nm [2]; dual beam oscilloscope

Transient formation:

$$OH + HO_2 \rightarrow H_2O_3, \quad pK_a(HO_2) = 4.69 \ [3]$$

$$9 < pK_a(H_2O_3) < 10 \ [4]$$

Footnotes:

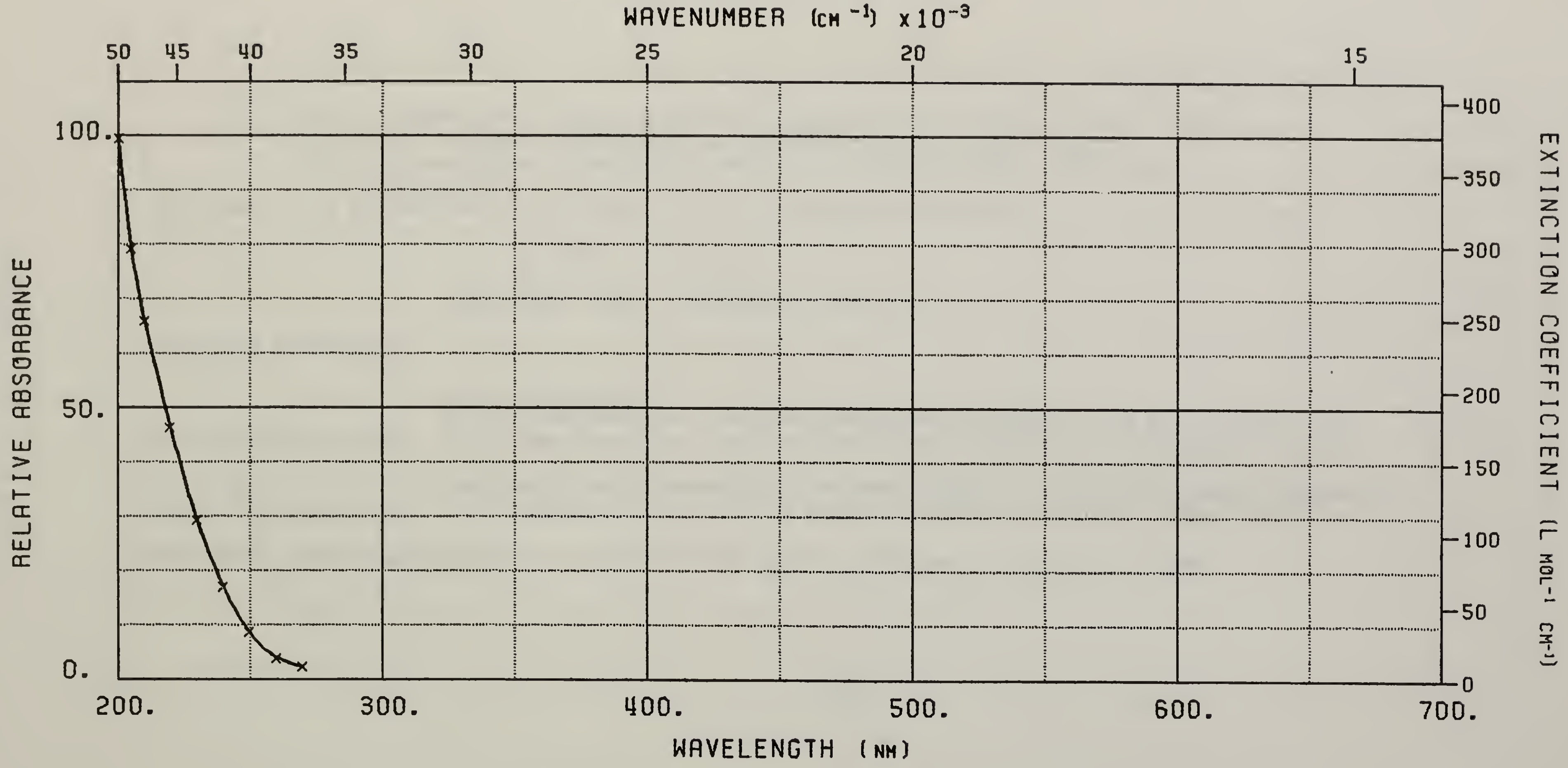
[1] Extinction coefficients were calculated using $G(H_2O_3) = 1.7$ from reference in footnote 4.

[2] Scattered light always kept below 2% of the analyzed light beam.

[3] B.H.J. Bielski, Photochem. Photobiol. 28(4-5): 645-9 (1978).

[4] G. Czapski and B.H.J. Bielski, J. Phys. Chem. 67(10): 2180-4 (1963).

D_2O_3



Transient [1]: D_2O_3, deuterium sesquioxide

System: oxygenated D_2O [1]

D_2O_3

Reference: B.H.J. Bielski, J. Phys. Chem. 74(17): 3213-6 (1970)

Transient generation: pulse radiolysis using 1.95 MeV Van de Graaff generator; pulse length 0.1 s [2]; dosimetry-ferrous sulfate

Spectral acquisition: deuterium monitoring lamp; 3-pass Suprasil quartz cell with optical path = 6.1 cm; two tandem coupled Bausch & Lomb f/3.5 monochromators [3]; 7200 RCA PMT

Transient formation:

$$D + O_2 \rightarrow DO_2$$

$$e(sol)^- + O_2 \rightarrow O_2^-$$

$$D^+ + O_2^- \rightarrow DO_2$$

$$OD + DO_2 \rightarrow D_2O_3$$

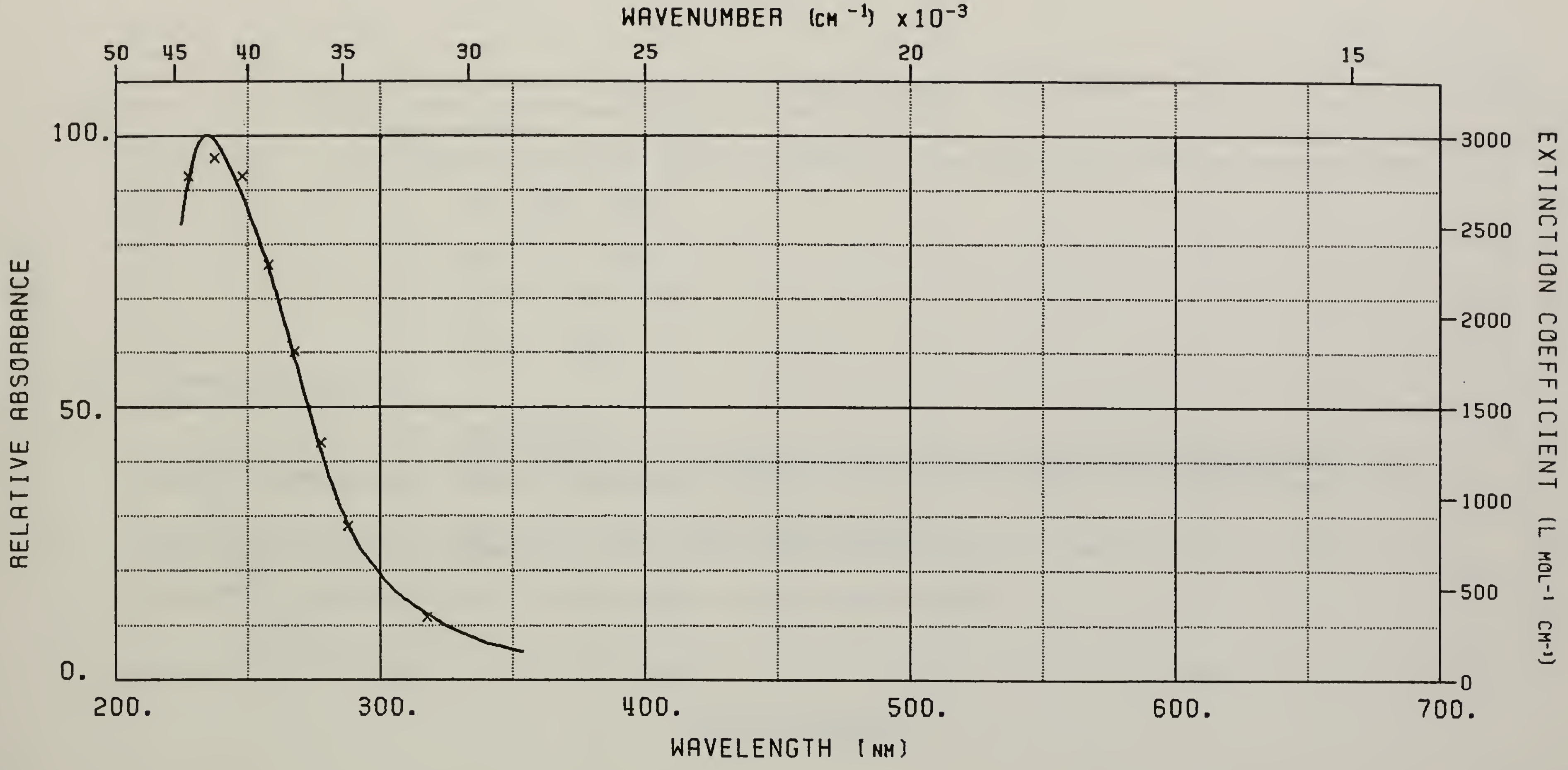
Footnotes:

[1] Extinction coefficient based on $G(D_2O_3) = 1.86$ which was determined in a 10^{-2} mol L^{-1} $DClO_4$ solution.

[2] Spectrum corresponds to time at end of pulse.

[3] Scattered light at 200 nm was < 0.3% of total light signal.

CO_2^-



Transient [1]: CO_2^-, carboxyl radical, $\lambda(max) = 235$ nm, $\epsilon_{235} = 3000$ L mol^{-1} cm^{-1} [2,3]

System: aqueous solution of 3×10^{-2} mol L^{-1} $HCOO^-$, 1 atm N_2O, pH 9

CO_2^-

Reference: P. Neta, M. Simic, and E. Hayon, J. Phys. Chem. 73(12): 4207-13 (1969)

Transient generation: pulse radiolysis, using Febetron 705; pulse energy 2.3 MeV; pulse length ≈ 30 ns; dose per pulse 8 krad; dosimetry 0.1 mol L^{-1} SCN^- solution [4]

Spectral acquisition: Osram XBO 450 W xenon lamp (pulsed); two high-intensity Bausch & Lomb monochromators, used in series to reduce scattered light [5]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH^- + OH$$

$$HCO_2^- + OH \rightarrow CO_2^- + H_2O, \ pK_a(HCOOH) = 3.77$$

$$HCO_2^- + H \rightarrow CO_2^- + H_2$$

Footnotes:

[1] Smooth curve for spectrum is from a composite spectrum.

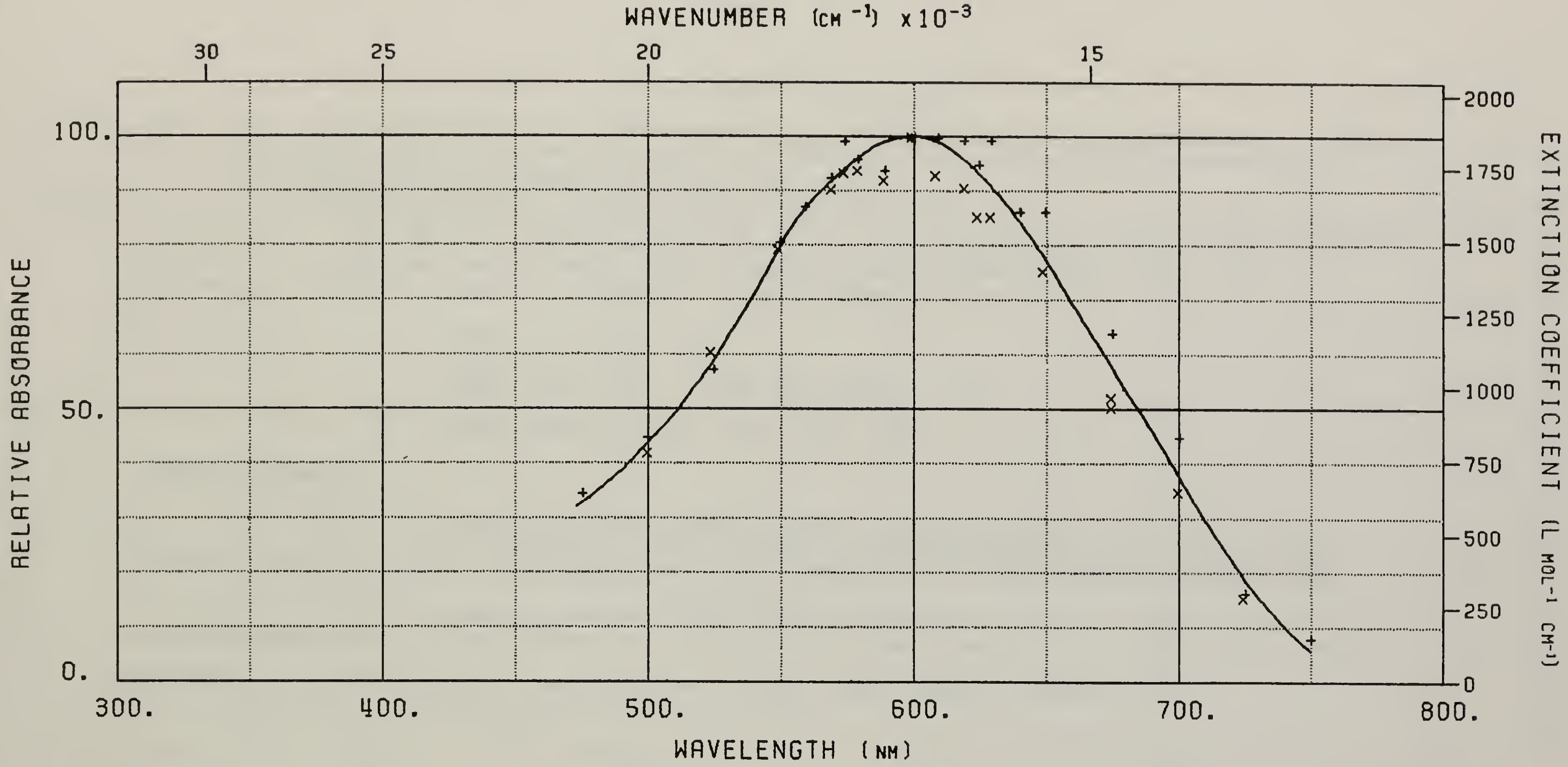
[2] Earlier results gave $\lambda(max) = (250 \pm 5)$ nm and $\epsilon_{250} = 2400$ L mol^{-1} cm^{-1}. J.P. Keene, Y. Raef, and A.J. Swallow, Pulse Radiolysis, M. Ebert, J.P. Keene, A.J. Swallow, and J.H. Baxendale (eds.), Academic Press, London, 1965, pp.99-106.

[3] Using $G(e(aq)^-) = G(OH) = 2.8$; deviation ± 15%.

[4] Using $\epsilon_{500} = 7600$ L mol^{-1} cm^{-1} for $(SCN)_2^-$.

[5] At 230 and 210 nm the amount of scattered light was 1% and 18%, respectively. M. Simic, P. Neta, and E. Hayon, J. Phys. Chem. 73(11): 3794-800 (1969).

CO_3^- or HCO_3



Transient: CO_3^- or HCO_3 [1], $\lambda(\max)$ = 600 nm, ϵ_{600} = 1860 L mol^{-1} cm^{-1} [2]

System: the chemical system represented by the data points "x" was an aqueous solution of 1 mol L^{-1} $NaHCO_3$, 10^{-3} mol L^{-1} H_2O_2, N_2-saturated, pH 8; and the system represented by the data points "+" was an aqueous solution of 1 mol L^{-1} Na_2CO_3, 2 x 10^{-4} mol L^{-1} H_2O_2, N_2-saturated, pH 13

CO_3^- or HCO_3

Reference: D. Behar, G. Czapski, and I. Duchovny, J. Phys. Chem. 74(10): 2206-10 (1970)

Transient generation [3]: flash photolysis, four O_2-filled (5 mm Hg) Spectrosil grade quartz lamps operated at 20 kV and 2 μF fired through a triggered spark gap

Spectral acquisition [3]: monitoring light was 120 W tungsten lamp; two 9558B EMI PMT; split beam technique; two Bausch 8 Lomb monochromators types 567 AB and F.D. 999

Transient formation [4]:

$$H_2O_2 + h\nu \rightarrow 2OH$$

$$OH^- + OH \rightleftharpoons O^- + H_2O, \; pK_a(OH) = 11.85$$

$$OH + CO_3{}^{2-} \rightarrow CO_3^- + OH^-$$

$$O^- + CO_3{}^{2-} \; (+H_2O) \rightarrow CO_3^- + 2OH^-$$

$$OH + HCO_3^- \rightarrow CO_3^- + H_2O$$

Footnotes:

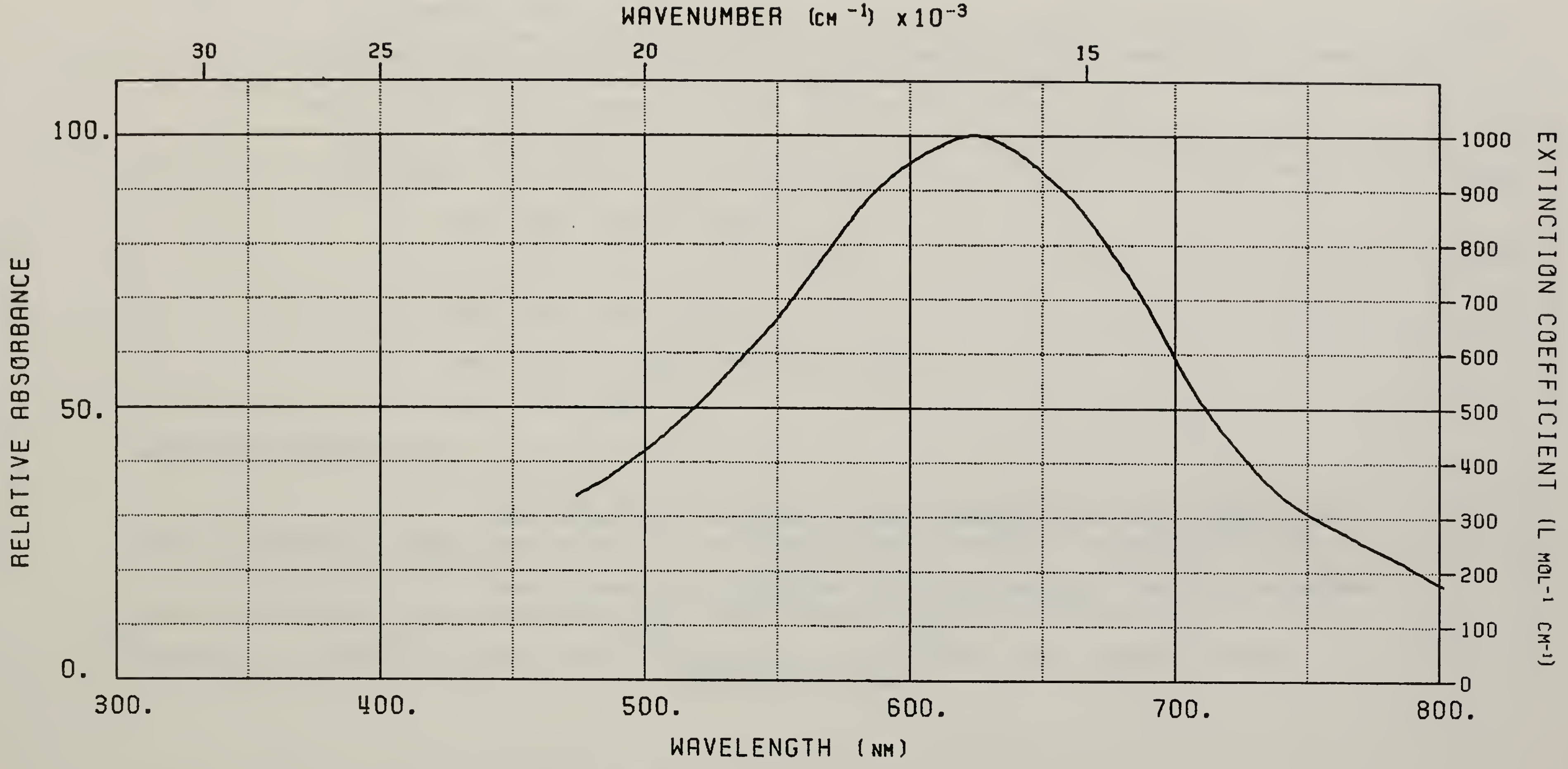
[1] $pK_a(HCO_3) = 9.6 \pm 0.3$; S. Chen, V.W. Cope, and M.Z. Hoffman, J. Phys. Chem. 77(9): 1111-6 (1973). These authors reported no difference between the spectra of HCO_3 and CO_3^-.

[2] J.L. Weeks and J. Rabani, J. Phys. Chem. 70(7): 2100-6 (1966).

[3] D. Behar and G. Czapski, Israel J. Chem. 6: 43-51 (1968).

[4] By measuring the rate constants in a pulse radiolysis experiment, it was found that reactions of OH with H_2O_2 to form O_2^- or HO_2 were negligible under the experimental conditions.

SiO_3^-



Transient: SiO_3^-, $\lambda(max)$ = 625 nm, $\epsilon = 1.0 \times 10^3$ L mol^{-1} cm^{-1}

System: aqueous solution of 5×10^{-2} mol L^{-1} Na_2SiO_3 and 1×10^{-2} mol L^{-1} $Na_2S_2O_8$

SiO_3^-

Reference: V.A. Kuz'min and A.K. Chibisov, High Energy Chem. 4(2): 146-7 (1970)

Transient generation: flash photolysis

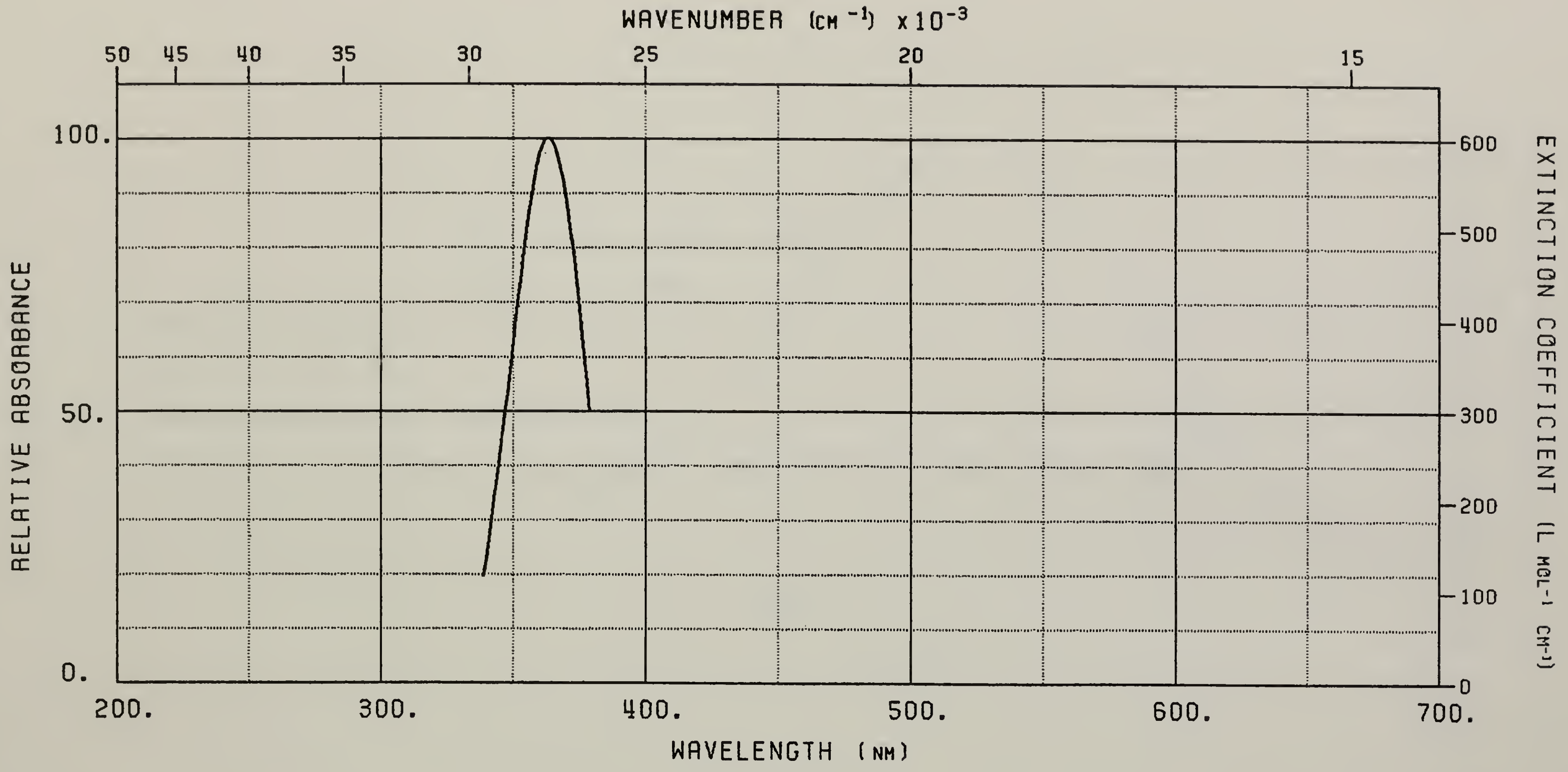
Spectral acquisition:

Transient formation:

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^-$$

$$SO_4^- + SiO_3^{2-} \rightarrow SO_4^{2-} + SiO_3^-$$

SO_2^-



Transient [1]: $\cdot SO_2^-$, $\lambda(max) \approx 365$ nm, $\epsilon_{365} \approx 600$ L mol^{-1} cm^{-1} [2,3],
$2k = 1.0 \times 10^{10}$ L mol^{-1} s^{-1}

System: aqueous solution of 6.0×10^{-2} HSO_3^-, N_2 (1 atm), pH 4.0

SO_2^-

Reference: E. Hayon, A. Treinin, and J. Wilf, J. Am. Chem. Soc. 94(1): 47-57 (1972)

Transient generation: flash photolysis; 1800 J; duration at "1/e" time of 5 μs; total pulse length 70 μs; 240 nm cutoff filter [4]

Spectral acquisition: Bausch & Lomb grating monochromator; PMT; spectrum was obtained by a point-by-point method from oscilloscope traces; each point was average of 3 or more experiments; time delay 80 μs after pulse

Transient formation [4]:

$$2HSO_3 \rightleftharpoons S_2O_5^{2-} + H_2O$$

$$^-O_3S\text{-}SO_2^- + h\nu \rightarrow SO_3^- + SO_2^-$$

Footnotes: [1] Spectrum obtained by subtracting contribution of $S_2O_4^{2-}$ formed from

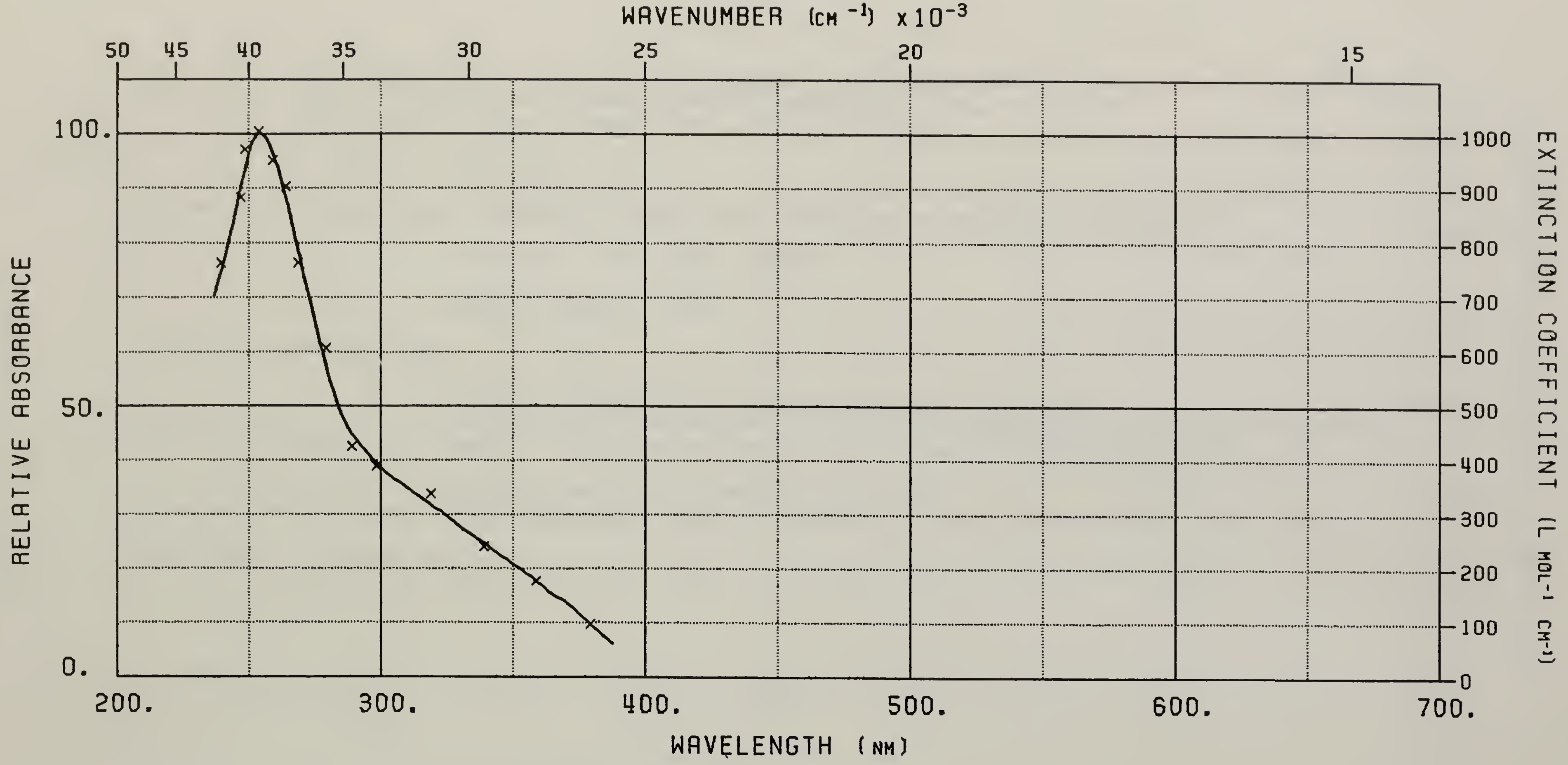
$$2SO_2^- \rightarrow S_2O_4^{2-}.$$

[2] Based on $\epsilon(max) = 8300$ L mol^{-1} cm^{-1} for $S_2O_4^{2-}$.

[3] Displayed spectrum normalized to 600 L mol^{-1} cm^{-1} at 363 nm.

[4] Cutoff filter permitted only $S_2O_5^{2-}$ to be photolyzed.

SO_3^-



Transient [1,2]: SO_3^-, λ(max) = 255 nm, $\epsilon_{255} \approx 1000$ L mol^{-1} cm^{-1}, 2k = (1.1 ± 0.2) x 10^{9} L mol^{-1} s^{-1}

System: aqueous solution of 2 x 10^{-3} mol L^{-1} SO_3^{2-}, N_2O-saturated, pH 10.3

SO_3^-

Reference: E. Hayon, A. Treinin, and J. Wilf, J. Am. Chem. Soc. 94(1): 47-57 (1972)

Transient generation: pulse radiolysis, using Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length ≈ 30 ns; dosimetry - N_2O-saturated, aqueous solution of KSCN [3]

Spectral acquisition: Osram XBO 450 W xenon lamp (pulsed); two high intensity Bausch & Lomb monochromators, used in series to reduce scattered light [4]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope

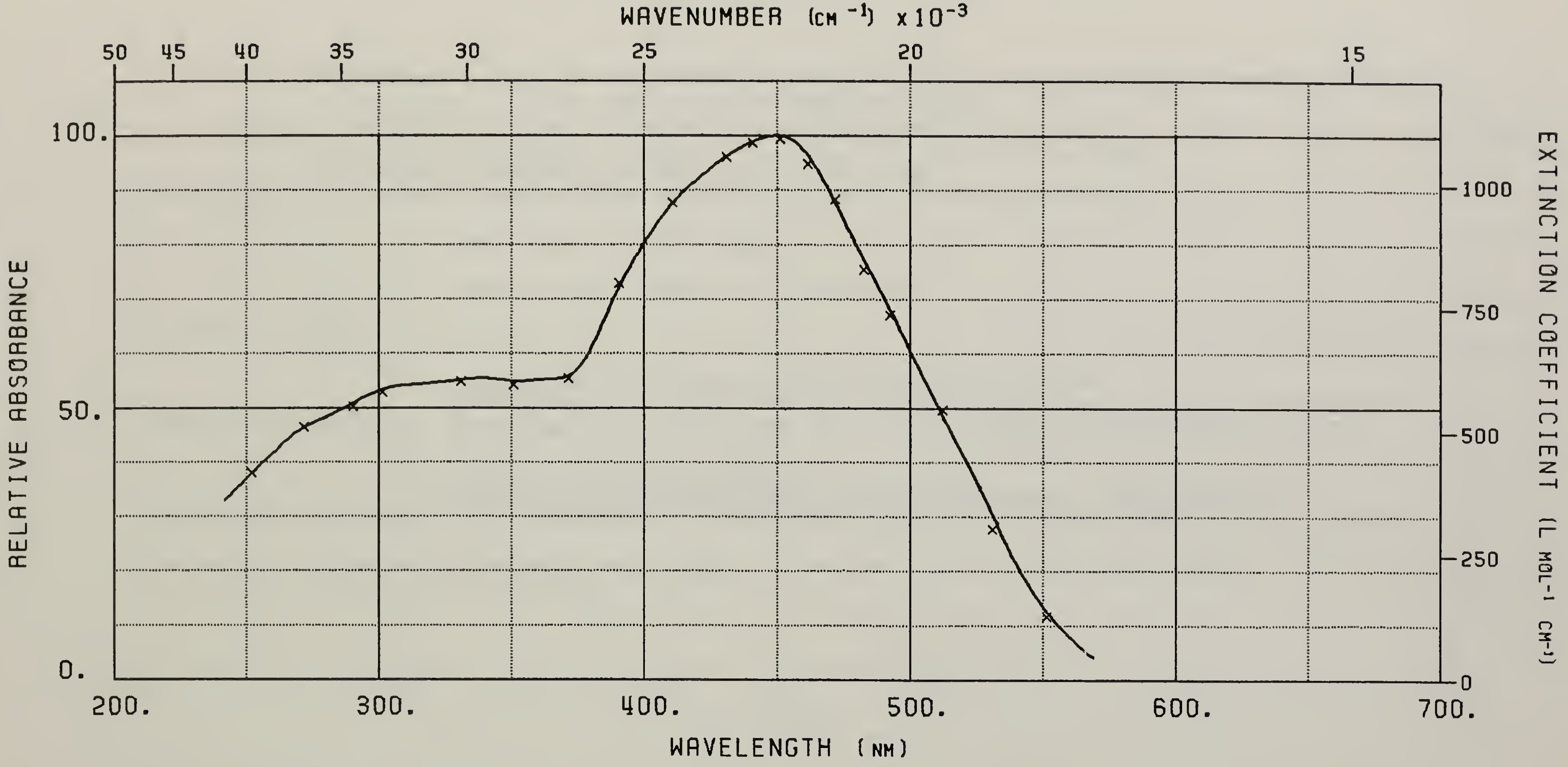
Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + SO_3{}^{2-} \rightarrow SO_3{}^- + OH^-$$

Footnotes:
[1] Points in spectrum are averages of three or more experiments.
[2] Spectrum remains unchanged in pH range 4-10.
[3] Using ϵ_{500} $(SCN)_2{}^-$ = 7600 L mol^{-1} cm^{-1} for 10^{-1} mol L^{-1} SCN^-, N_2O-saturated solutions at pH 5.5 and assuming $G = G(e(aq)^-) + G(OH) = 5.5$, E. Hayon, J. Chem. Phys. 51(11): 4881-92 (1969).
[4] At 230 and 210 nm, the amount of scattered light was 1% and 18%, respectively.

SO_4^-



Transient: SO_4^-, sulfate radical anion, λ(max) = 450 nm [1] , ϵ_{450} = 1100 L mol^{-1} cm^{-1} [1,2]

System: aqueous solution of 2×10^{-3} mol L^{-1} $S_2O_8^{2-}$, Ar(1 atm), pH = 5.1

SO_4^-

Reference: E. Hayon, A. Treinin, and J. Wilf, J. Am. Chem. Soc. 94(1): 47-57 (1972)

Transient generation: electrons from Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length ≈ 30 ns; dosimetry [3] N_2O-saturated aqueous solution of 0.1 mol L^{-1} SCN^- at pH 5.5

Spectral acquisition: Osram XBO W xenon lamp; two high-intensity Bausch & Lomb monochromators used in series to reduce scattered light; two EMI 9558QB PMT; dual beam Fairchild 777 oscilloscope; quartz cells with optical path lengths of 2 cm; spectrum is the average of 3 runs.

Transient formation:

$$S_2O_8^{2-} + e(aq)^- \rightarrow SO_4^{2-} + SO_4^-$$

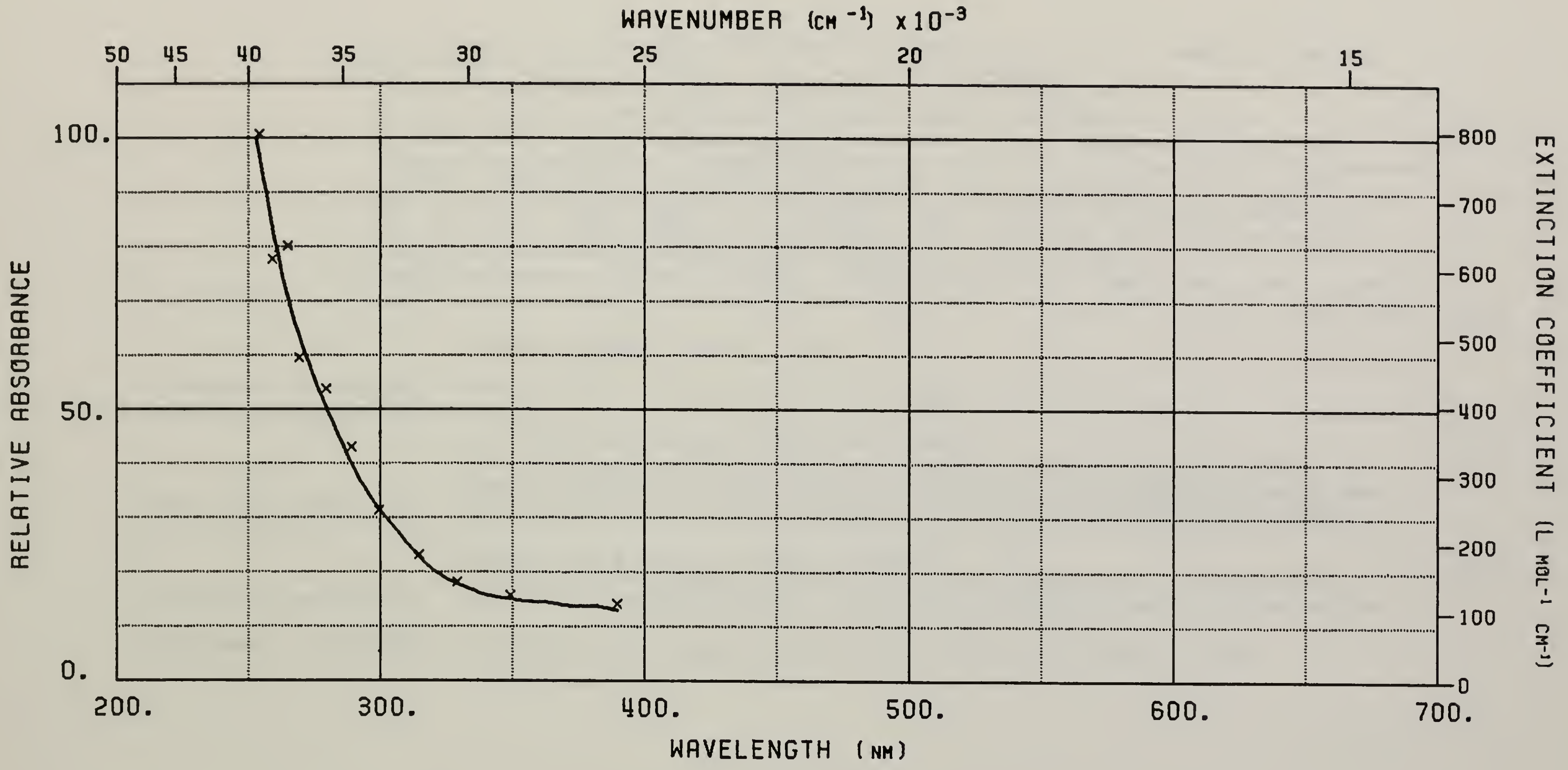
Footnotes:

[1] With spectrum of SO_4^- displayed, Hayon, Treinin, and Wilf quoted (but apparently did not measure) a value of $\lambda(max) = 450$ nm and $\epsilon_{450} = 1100$ L mol^{-1} cm^{-1}. The displayed spectrum is normalized to conform to these values.

[2] The extinction coefficient was measured by W. Roebke, M. Renz, and A. Henglein, Int. J. Radiat. Phys. Chem. 1(1): 39-44 (1969). They reported the maximum of the SO_4^- spectrum to be at $\lambda(max) = 460$ nm. Earlier values of extinction coefficients were $\epsilon_{455} = (450 \pm 45)$ L mol^{-1} cm^{-1} from E. Hayon and J.J. McGarvey, J. Phys. Chem. 71(5): 1472-7 (1967) and $\epsilon_{455} = (460 \pm 25)$ L mol^{-1} cm^{-1} from L. Dogliotti and E. Hayon, J. Phys. Chem. 71(8): 2511-6 (1967). In these last two references, $\lambda(max)$ was quoted at 455 nm.

[3] Using $\epsilon_{500}((SCN)_2^-) = 7600$ L mol^{-1} cm^{-1} and assuming $G = G(e(aq)^-) + G(OH) = 5.5$, E. Hayon, J.Chem. Phys. 51(11): 4881-92 (1969).

SO_5^-



Transient [1]: SO_5^-, $\epsilon_{265} \approx 560$ L mol^{-1} cm^{-1} [2]

System: aqueous solution of 2×10^{-3} mol L^{-1} HSO_5^-, N_2O-saturated, pH ≈ 6

SO_5^-

Reference: E. Hayon, A. Treinin, and J. Wilf, J. Am. Chem. Soc. 94(1): 47-57 (1972)

Transient generation: pulse radiolysis, using Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length ≈ 30 ns; dosimetry - N_2O-saturated, aqueous solution of KSCN [3]

Spectral acquisition: Osram XBO 450 W xenon lamp (pulsed); two high intensity Bausch & Lomb monochromators, used in series to reduce scattered light [4]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope; time delay 200 μs after pulse

Transient formation:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow N_2 + OH^- + OH$$

$$OH + HSO_5^- \rightarrow OH^- + HSO_5\ (\text{or } SO_5^-)$$

Footnotes:

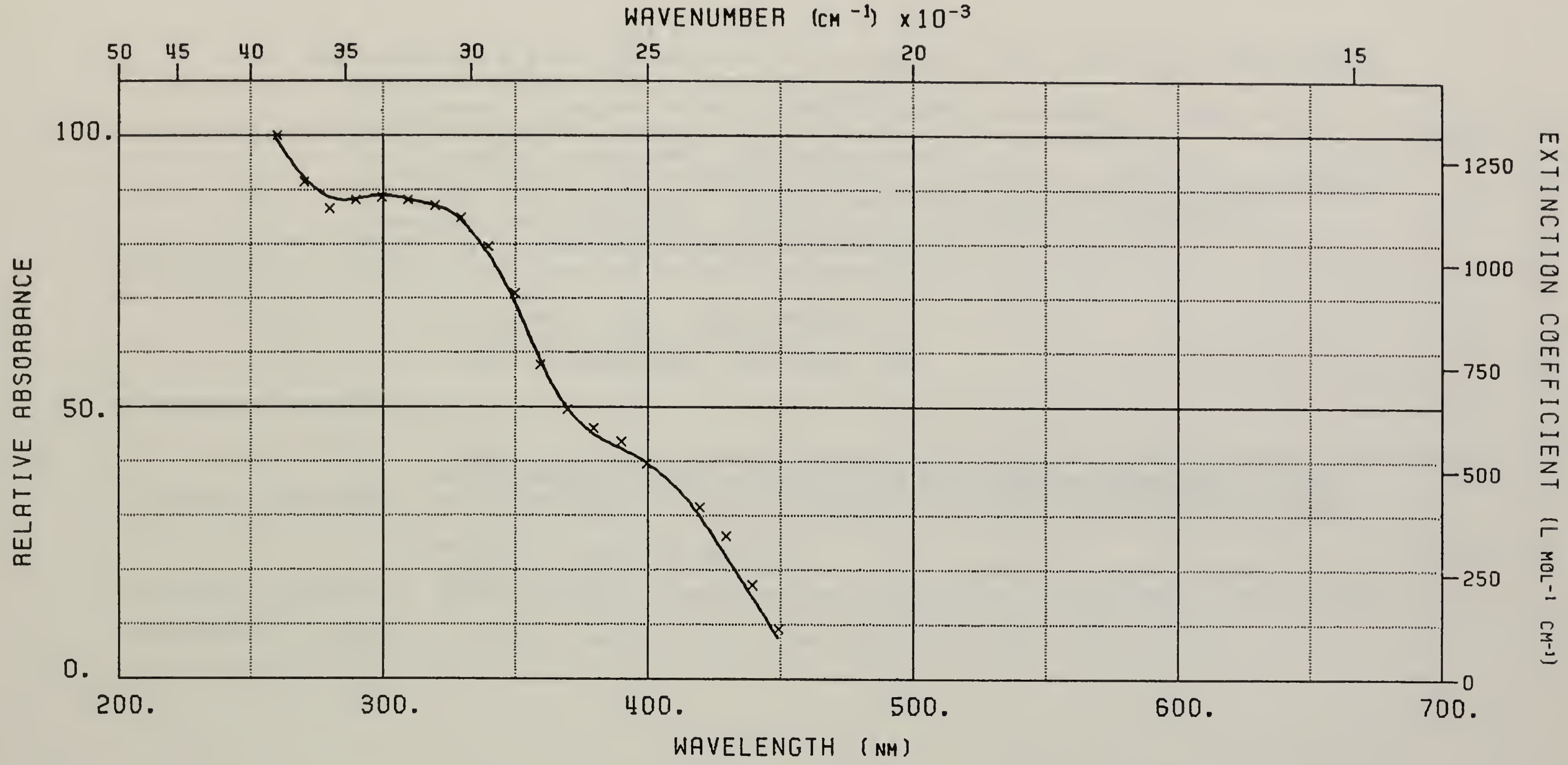
[1] Points in spectrum are averages of three of more experiments.

[2] Quoted extinction coefficient is a lower limit. Impurities, sulfates, H_2O_2, and $S_2O_8^{2-}$, in the prepared salts $KHSO_5$ and $NaHSO_4$ made ϵ uncertain. Earlier values of $\epsilon\ (SO_5^-)$ and the shape of earlier spectra were somewhat different, W. Roebke, M. Renz, and A. Henglein, Int. J. Radiat. Phys. Chem. 1(1): 39-44 (1969).

[3] Using $\epsilon_{500}\ (SCN)_2^- = 7600$ L mol^{-1} cm^{-1} for 10^{-1} mol L^{-1} SCN^-, N_2O-saturated solutions at pH 5.5 and assuming $G = G(e(aq)^-) + G(OH) = 5.5$, E. Hayon, J. Chem. Phys. 51(11): 4881-92 (1969).

[4] At 230 and 210 nm, the amount of scattered light was 1% and 18%, respectively.

$S_2O_3^-$



Transient [1]: $S_2O_3^-$ [2]

System: aqueous solution of 10^{-4} mol L^{-1} $S_2O_3^{2-}$, saturated with N_2O, pH = 4.8

$S_2O_3^-$

Reference: M. Schoeneshoefer, Int. J. Radiat. Phys. Chem. 5: 375-86 (1973)

Transient generation: pulse radiolysis [3] using Van de Graaff generator; energy 1.5 MeV; dose rate during the pulse was 700 rad per μs

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay-immediately after pulse

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + S_2O_3^{2-} \rightarrow S_2O_3^- + OH^-$$

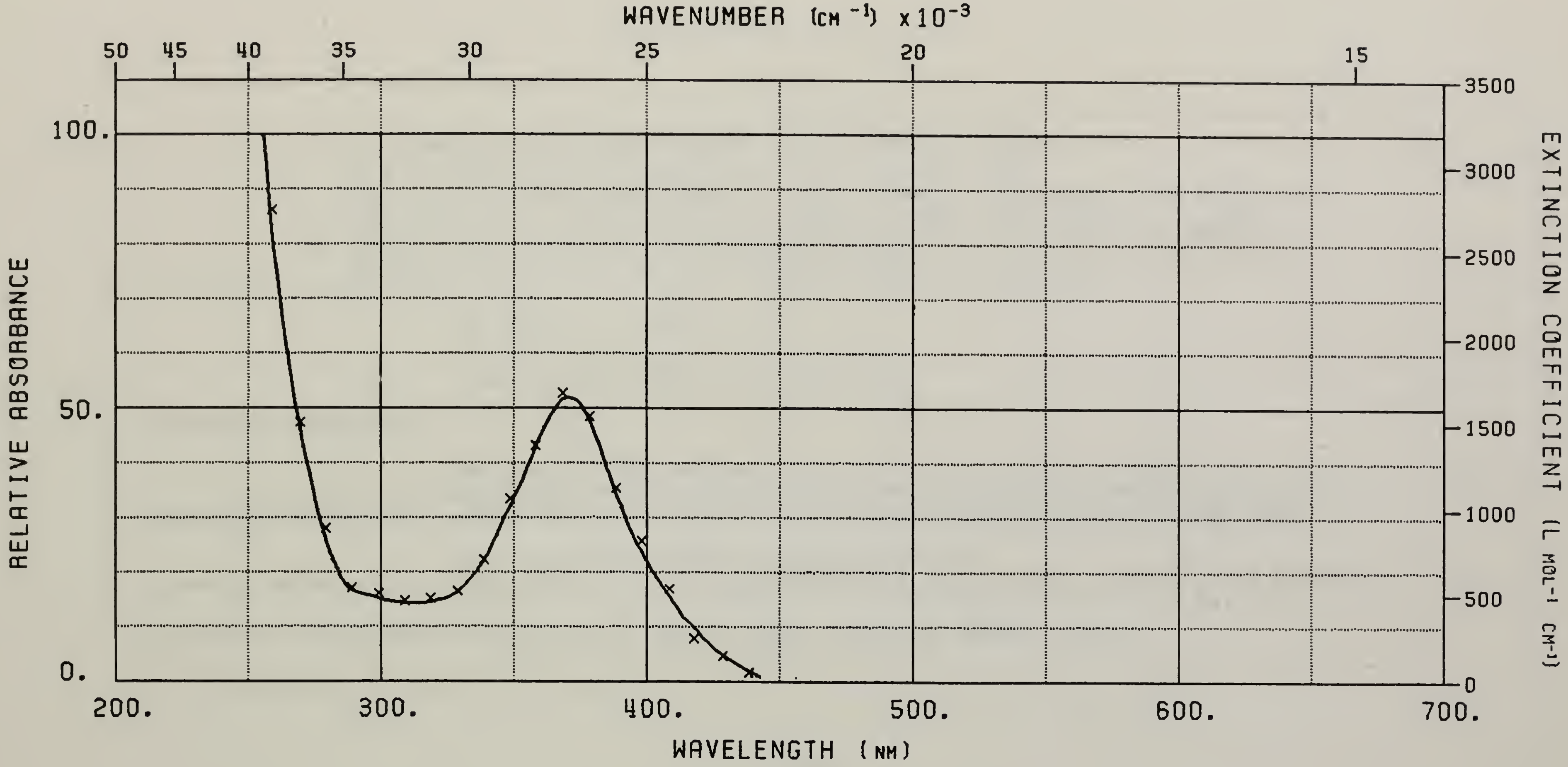
Footnotes:

[1] Spectrum corrected for $S_2O_3^- + S_2O_3^{2-} \rightleftharpoons S_4O_6^{3-}$ equilibrium. Extinction coefficients were based on G(OH) = 6.

[2] Another spectrum has been assigned as the $S_2O_3^-$ spectrum: L. Dogliotti and E. Hayon, J. Phys. Chem. 72: 1800-7 (1968); G.E. Adams, J.W. Boag, and B.D. Michael, Proc. Chem. Soc. 411 (1964); G.E. Adams, J.W. Boag, and B.D. Michael, Trans. Faraday Soc. 61: 1674-80 (1965).

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

$S_4O_6H^{2-}$ ($S_4O_6^{3-}$)



Transient: $S_4O_6H^{2-}$ [1] ($S_4O_6^{3-}$ [2]), λ(max) = 370 nm, ϵ_{370} = 1650 L mol^{-1} cm^{-1} [3], $2k = 1.1 \times 10^9$ L mol^{-1} s^{-1}

System: aqueous solution of 10^{-4} mol L^{-1} $S_2O_3^{2-}$, saturated with N_2O, pH = 4.8

$S_4O_6H^{2-}$ ($S_4O_6^{3-}$)

Reference: M. Schoeneshoefer, Int. J. Radiat. Phys. Chem. 5: 375-86 (1973)

Transient generation: pulse radiolysis [4] using Van de Graaff generator; energy 1.5 MeV; dose rate during the pulse was 700 rad per μs

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay-spectrum measured after 25 μs and extrapolated to time zero

Transient formation [5]:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + S_2O_3^{2-} \rightarrow S_2O_3^- + OH^-$$

$$S_2O_3^- + S_2O_3^{2-} \rightarrow S_4O_6^{3-}$$

$$S_4O_6^{3-} + H^+ \rightleftharpoons S_4O_6H^{2-}, \ pK_a(S_4O_6H^{2-}) \approx 6$$

Footnotes:

[1] Similar spectra have been attributed to the $S_2O_3^-$ radical: L. Dogliotti and E. Hayon, J. Phys. Chem. 72: 1800-7 (1968); G.E. Adams, J.W. Boag, and B.D. Michael, Proc. Chem. Soc. 411 (1964); G.E. Adams, J.W. Boag, and B.D. Michael, Trans. Faraday. Soc. 61: 1674-80 (1965).

[2] Spectrum is almost independent of pH.

[3] Using G(OH) = 6.

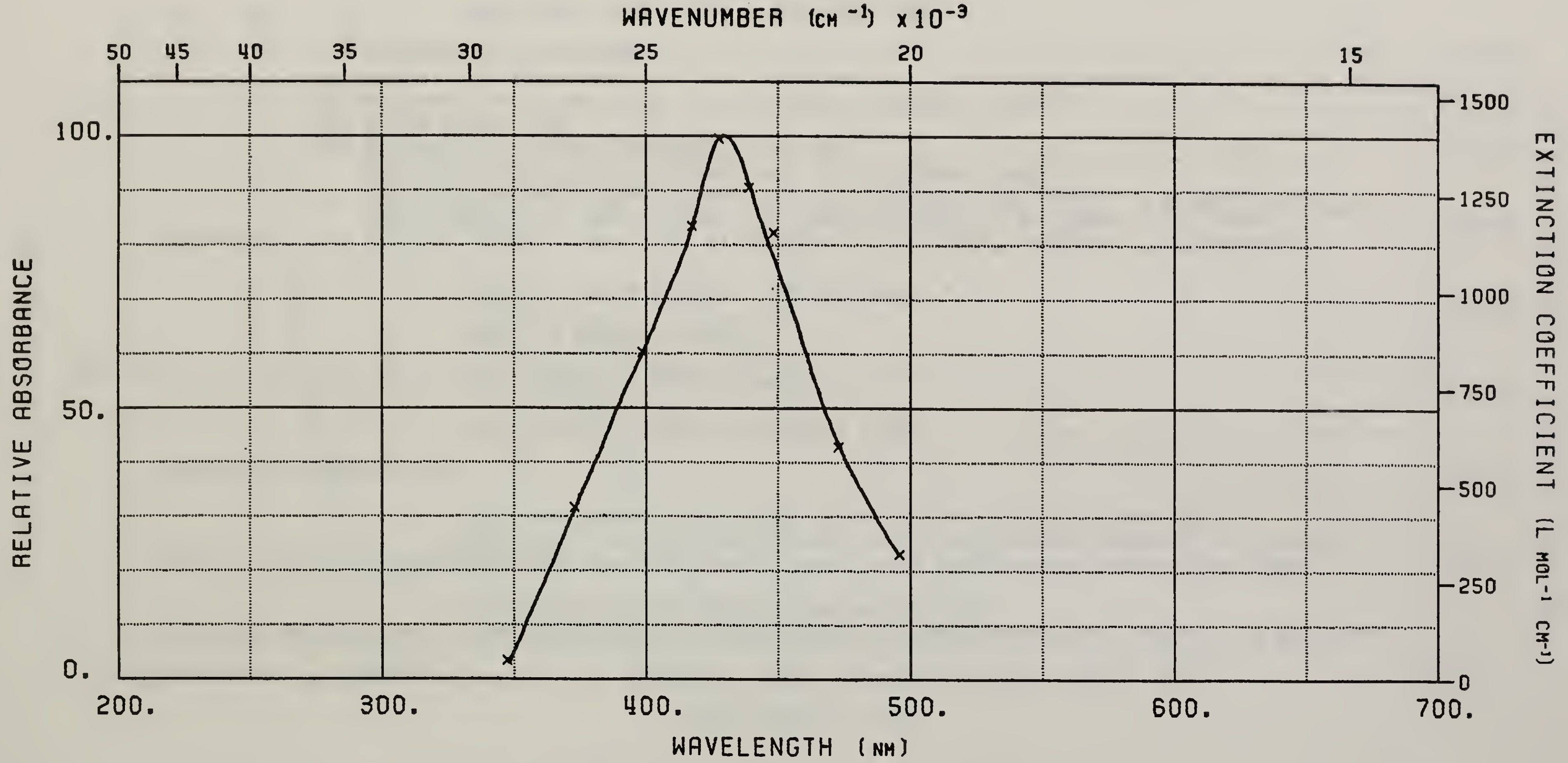
[4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[5] Almost identical spectrum was obtained in an alkaline, aqueous solution of $S_4O_6^{2-}$, containing tert-butanol.

$$(CH_3)_3COH + OH \rightarrow H_2O + CH_2C(CH_3)_2OH$$

$$e(aq)^- + S_4O_6^{2-} \rightarrow S_4O_6^{3-}$$

SeO_3^-



Transient: SeO_3^-, λ(max) = 430 nm, ϵ_{430} = 1.4 x 10^3 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 10^{-2} mol L^{-1} SeO_3^{2-}, Ar-saturated, pH natural

SeO_3^-

Reference: M.S. Subhani and T. Kausar, Rev. Roum. Chim. 23(11-12): 1627-30 (1978)

Transient generation: flash photolysis, using flash tubes [2]

Spectral acquisition: monitoring lamp; monochromator; PMT; oscilloscope [3]

Transient formation:

$$SeO_3^{2-}\ H_2O + h\nu \rightarrow SeO_3^{2-}\ H_2O^*$$

$$SeO_3^{2-}\ H_2O^* \rightarrow SeO_3^- + e(aq)^-\ (+H_2O)$$

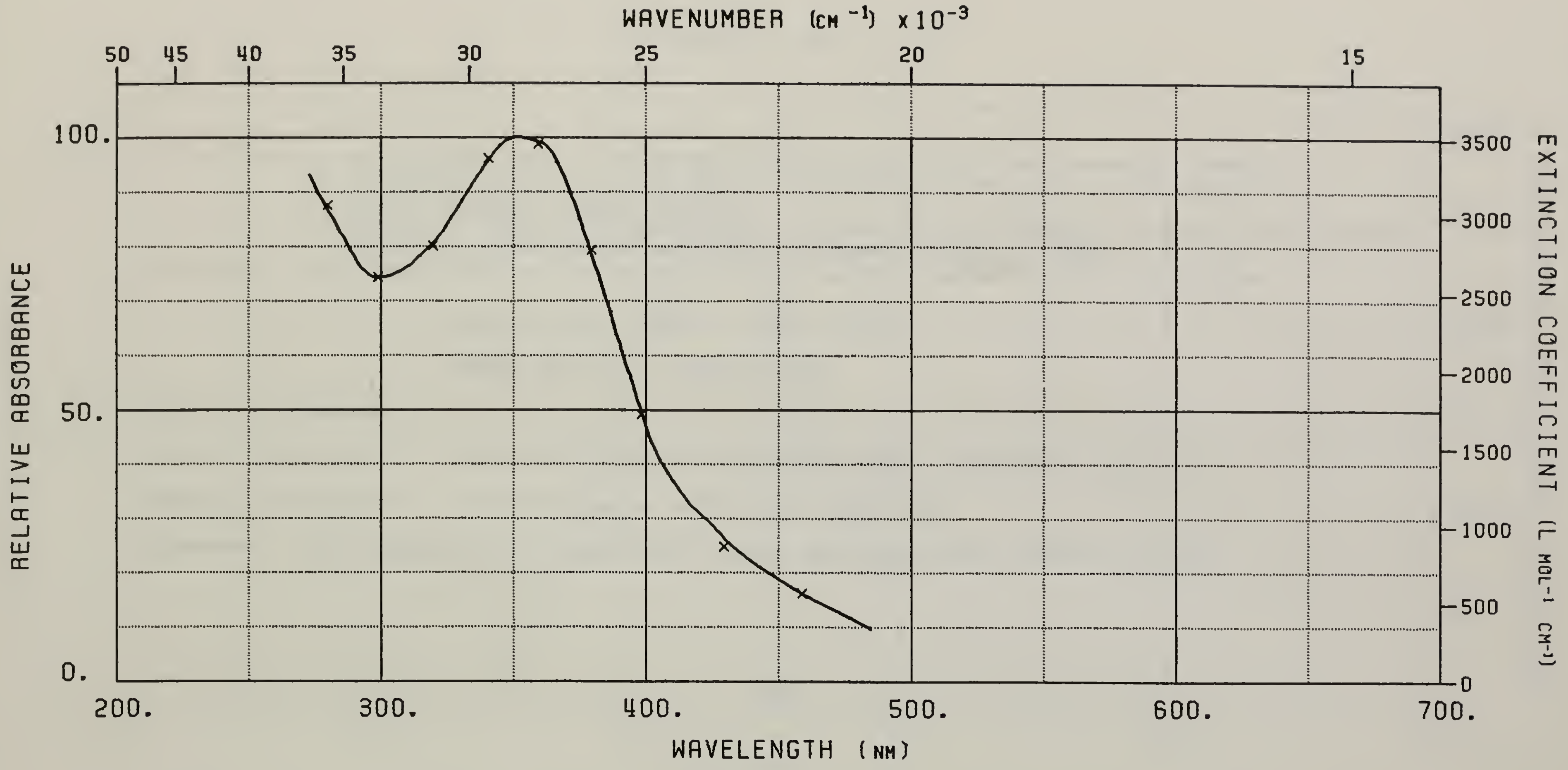
Footnotes:

[1] Extinction coefficient obtained by assuming amount of O_2^-, formed from $e(aq)^-$ in O_2-saturated solutions, is equal to that of SeO_3^-.

[2] Apparatus similar to that in G.V. Buxton and M.S. Subhani, J. Chem. Soc. Faraday Trans. 1 68(5): 958-69 (1972).

[3] Apparatus similar to that in K.W. Chambers, E. Collinson, F.S. Dainton, W.A. Seddon, and F. Wilkinson, Trans. Faraday Soc. 63: 1699-711 (1967).

TeO_3^-



Transient: TeO_3^-, λ(max) = 350 nm, ε = 3500 L mol^{-1} cm^{-1}

System: aqueous solution of 2 x 10^{-2} mol L^{-1} TeO_3^{2-}, air-saturated, pH neutral

TeO_3^-

Reference: G.E. Adams, J.W. Boag, and B.D. Michael, Trans. Faraday Soc. 61: 1674-80 (1965)

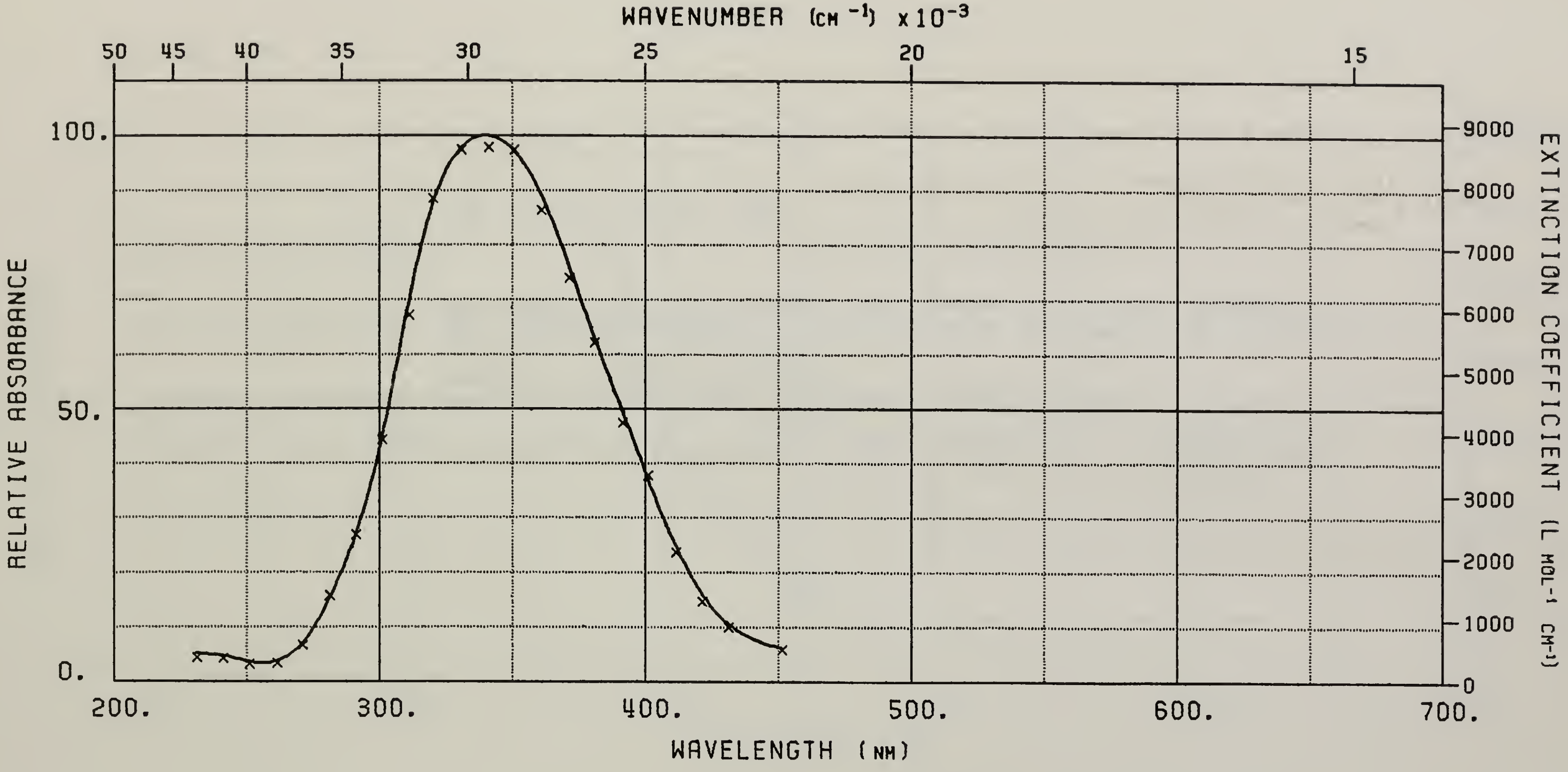
Transient generation: pulse radiolysis, linear accelerator; energy 1.8 MeV; dosimetry, using ferrocyanide

Spectral acquisition: 450 W xenon monitoring lamp; Bausch 8 Lomb type 250 grating monochromator; EMI 9558 QC PMT; 545 Tektronix oscilloscope with 53/54L preamplifier

Transient formation:

$$OH + TeO_3^{2-} \rightarrow TeO_3^- + OH^-$$

Cl_2^-



Transient: Cl_2^-, λ(max) = 340 nm, ϵ_{340} = (8800 ± 500) L mol^{-1} cm^{-1} [1,2]

System: aqueous solution of 10^{-2} mol L^{-1} Cl^-, Ar saturated, 10^{-1} mol L^{-1} perchloric acid, pH ≈ 1

Cl_2^-

Reference: G.G. Jayson, B.J. Parsons, and A.J. Swallow, J. Chem. Soc., Faraday Trans. 1 69: 1597-607 (1973)

Transient generation: pulse radiolysis, electron linear accelerator; dose per pulse 1.58 x 10^3 rad; dosimetry-secondary emission chamber [3]

Spectral acquisition: two Bausch & Lomb high-intensity monochromators used in series to reduce scattered light.

Transient formation:

$$OH + Cl^- \rightleftharpoons ClOH^-$$

$$ClOH^- + H^+ \rightarrow H_2O + Cl$$

$$Cl + Cl^- \rightleftharpoons Cl_2^-$$

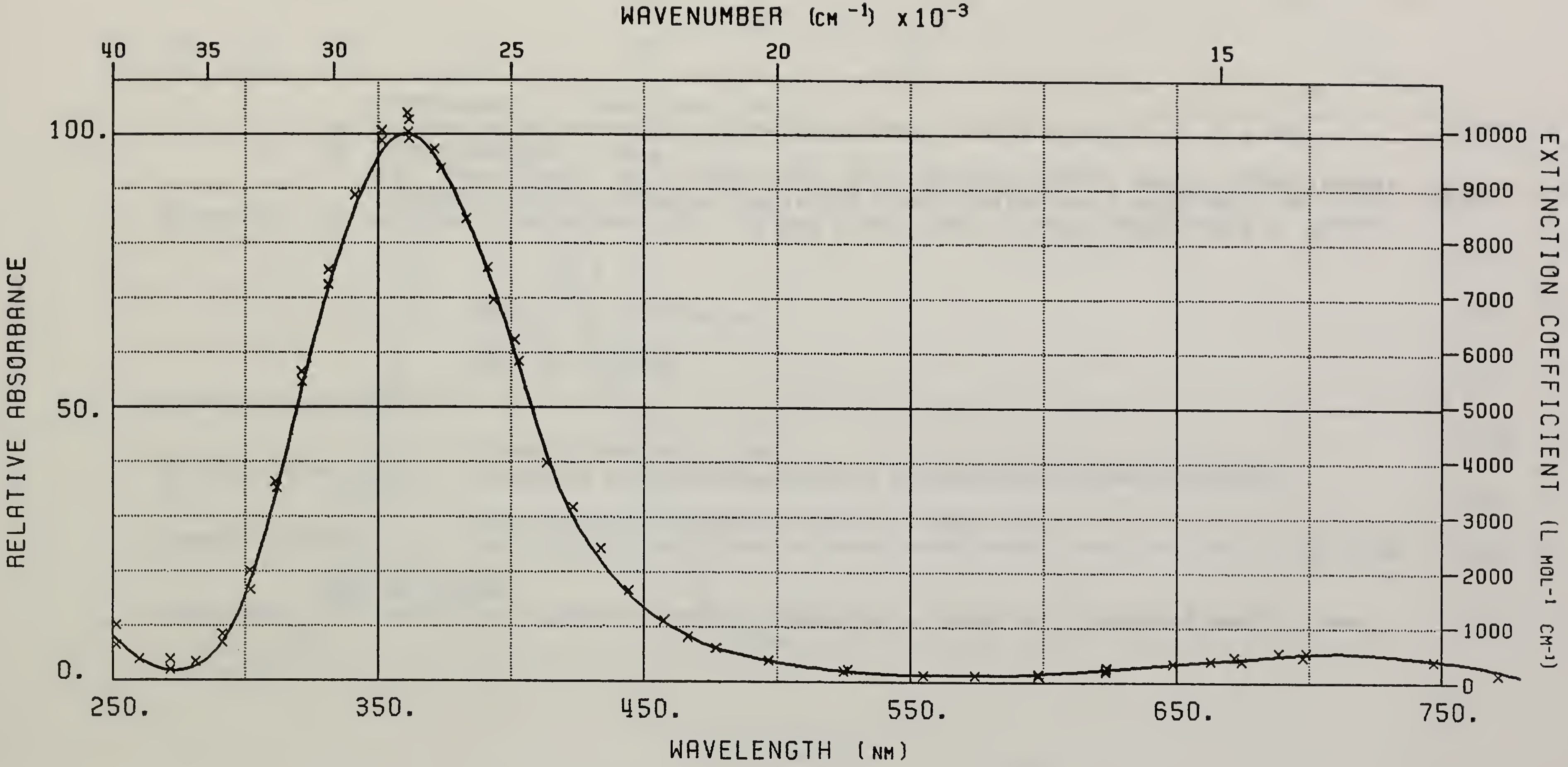
Footnotes:

[1] An earlier value was ϵ_{340} = 12,500 L mol^{-1} cm^{-1} from M. Anbar and J.K. Thomas, J. Phys. Chem. 68: 3829-35 (1964) and a later value was ϵ = 12,400 L mol^{-1} cm^{-1} from R.K. Broszkiewicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim. 24(2): 123-31 (1976).

[2] Assuming $G(Cl_2^-) = 2.9$.

[3] Calibrated by aqueous potassium thiocyanate taking $G((SCN)_2^-) = 2.9$ and $\epsilon_{500}((SCN)_2^-) = 7100$ L mol^{-1} cm^{-1}.

Br_2^-



Transient: Br_2^-, λ(max) = 360 nm, ϵ_{360} = (9900 ± 600) L mol^{-1} cm^{-1} [1,2]

System: aqueous solution of 10^{-3} mol L^{-1} Br^-, neutral, N_2O-saturated

Br_2^-

Reference: D. Zehavi and J. Rabani, J. Phys. Chem. 76(3): 312-9 (1972)

Transient generation: pulse radiolysis; energy 5 MeV; pulse length 0.1 μs; dosimetry-induction coil [3]

Spectral acquisition: split analyzing light beam with two monochromators; extrapolated to zero time; PMT's type R166 for 260-300 nm, 1P28 for 300-650 nm and R196 above 650 nm; dual-beam oscilloscope; filter used to prevent photolysis and second-order light; 150 W xenon lamp

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + Br^- \rightleftarrows BrOH^-$$

$$BrOH^- \rightarrow Br + OH^-$$

$$Br + Br^- \rightleftarrows Br_2^-$$

$$BrOH^- + Br^- \rightarrow Br_2^- + OH$$

Footnotes:

[1] D. Behar, private communication, 1980.

[2] Value quoted by authors was (12,000 ± 1000) L mol^{-1} cm^{-1}. However, other values for ϵ_{360} in the literature are lower. For example 9600 L mol^{-1} cm^{-1} [4], 8200 L mol^{-1} cm^{-1} [5], 8300 L mol^{-1} cm^{-1} [6], and 8560 L mol^{-1} cm^{-1} [7]. In addition ϵ_{365} = 7800 L mol^{-1} cm^{-1} [8].

[3] Internal dosimeter using Br_2^- absorption was also used.

[4] B. Cercek, M. Ebert, C.W. Gilbert, and A.J. Swallow, Pulse Radiolysis, eds. M. Ebert, J.P. Keene, A.J. Swallow, and J.H. Baxendale (Academic Press, 1965) p. 83.

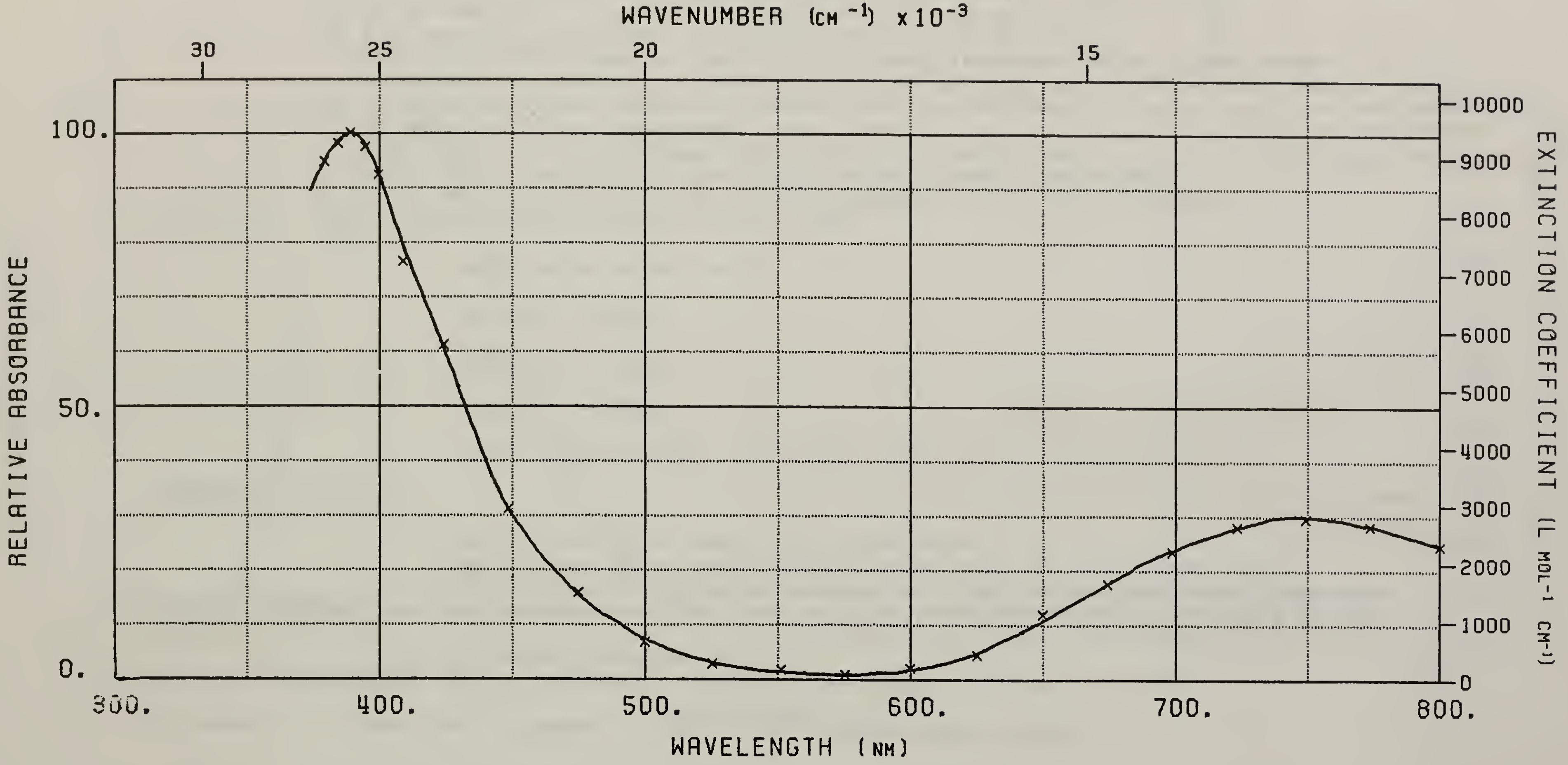
[5] H.C. Sutton, G.E. Adams, J.W. Boag, and B.D. Michael, ibid., p. 61.

[6] B. Cercek, Int. J. Radiat. Phys. Chem. 4(1): 25-30 (1972).

[7] R.K. Broszkiewicz, Bull. Acad. Pol. Sci. Chim. 24(2): 123-31 (1976).

[8] M.S. Matheson, W.A. Mulac, J.L. Weeks, J. Rabani, J. Phys. Chem. 70: 2092-9 (1966).

I_2^-



Transient [1]: I_2^-, $\epsilon(\max) \approx 9400$ L mol^{-1} cm^{-1} [2,3,4]

System: aqueous solution of 3.3×10^{-4} mol L^{-1} I^-, pH neutral, oxygen-saturated

I_2^-

Reference: R. Devonshire and J.J. Weiss, J. Phys. Chem. 72(11): 3815-20 (1968)

Transient generation: photolysis using the 185 nm mercury line from a low-pressure Spectrosil mercury lamp; photolyzing light intensity was modulated at 50 Hz by using a leakage reactance transformer giving 120 mA and 1650 V; pure N_2 was passed between the lamp and absorption cell

Spectral acquisition: absorption cell was a 50 cm Spectrosil tube of 0.5 cm inside diameter; monitoring lamp was 150 W quartz tungsten-iodine lamp using a 24 V battery; heat filter was used in monitoring beam [5]; the output from PMT was detected using phase sensitive technique using electronic components from Brookdeal Electronics Ltd. - amplifier (LA635), phase sensitive detector (PD629), phase shifter (PS946), and meter (MU947).

Transient formation:

$$I^- + h\nu \rightarrow (I^-)^*$$

$$(I^-)^* \rightarrow I + e^-$$

$$I^- + I \rightarrow I_2^-$$

Footnotes:

[1] At wavelengths shorter than about 525 nm, the spectrum has been corrected for the build-up of I_3^- from the photolysis.

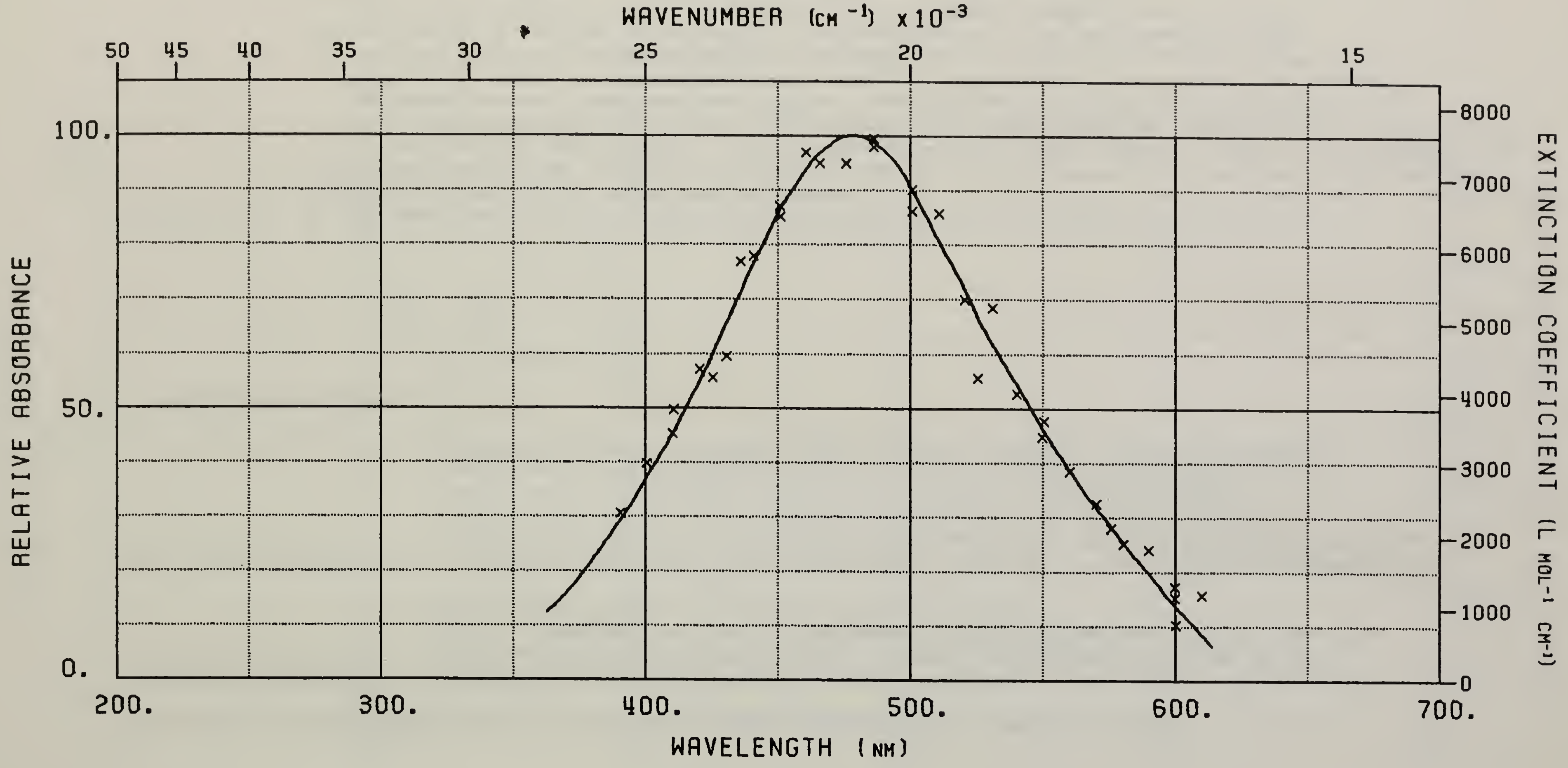
[2] Listed extinction coefficient of 9400 L mol^{-1} cm^{-1} is from a spectrum where the maximum extinction was near 380 nm. Private communication, R.H. Schuler, 1979. In contrast, the literature spectrum of I_2^-, after being digitized from the journal and smoothed, shows a maximum near 390 nm. For the purpose of this compilation, the literature spectrum is normalized to ϵ(max) = 9400 L mol^{-1} cm^{-1}; but the original wavelength scale is used, so that the displayed spectrum has λ(max) $\approx$ 390 nm.

[3] In deaerated aqueous solution L.I. Grossweiner and M.S. Matheson, J. Phys. Chem. 61: 1089-95 (1957), measured ϵ_{395} = (15,600 ± 3000) L mol^{-1} cm^{-1}.

[4] Ratio of absorbance at 390 nm to absorbance at 750 nm = 3.5.

[5] To further guard against large temperature fluctuations, the solutions were only irradiated for 30 s.

(SCN)$_2^-$



Transient: (SCN)$_2^-$, λ(max) = 480 nm [1], ϵ_{475} = 7600 L mol^{-1} cm^{-1} [2,3,4]

System: aqueous 10^{-4} mol L^{-1} KSCN (freshly prepared), N_2-saturated, pH 6.0

$(SCN)_2^-$

Reference: L. Dogliotti and E. Hayon, J. Phys. Chem. 72: 1800-1807 (1968)

Transient generation: flash photolysis; energy per pulse 1800 J; duration at "1/e time" of 5 μs; pulse length 70 μs

Spectral acquisition: Bausch & Lomb grating monochromator; EMI 9558QB photomultiplier; spectra were obtained by a point-by-point method; time delay = 80 μs after start of pulse

Transient formation:

$$SCN^- \cdot H_2O + h\nu \rightarrow SCN + e(aq)^- + H_2O$$

$$SCN + SCN^- \rightarrow (SCN)_2^-$$

Footnotes:

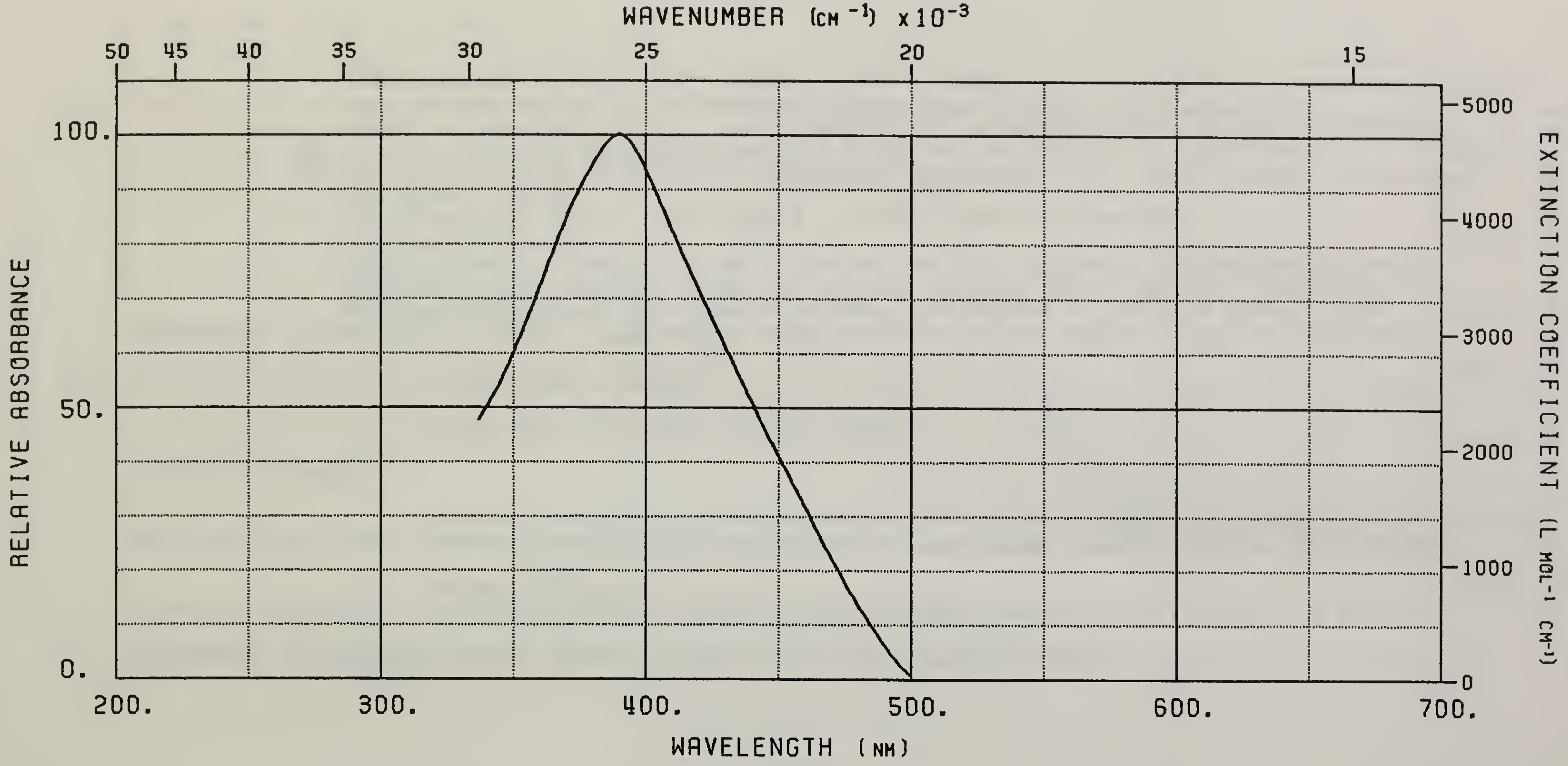
[1] A value of λ(max) = 485 nm was quoted by the authors. However, the digitization of spectrum showed that they apparently meant the maximum of the data points. The maximum of their smoothed curve was 478 nm. For the purpose of this compilation, 478 is rounded to 480 nm in the quoted maximum, but 478 nm is the maximum of the displayed spectrum.

[2] J.H. Baxendale, P.L.T. Bevan, and D.A. Stott, Trans. Faraday Soc. 64: 2389-97 (1968).

[3] The spectrum displayed has been normalized to correspond to ε(max) = 7600 L mol^{-1} cm^{-1}.

[4] A recent spectrum of $(SCN)_2^-$ has been taken and shows λ(max) = 472 nm and ε(max) = 7580 L mol^{-1} cm^{-1}. The G($(SCN)_2^-$) was measured to be 6.13 in 10^{-2} mol L^{-1} SCN^- aqueous solutions, saturated with N_2O. R.H. Schuler, L.K. Patterson, and E. Janata, J. Phys. Chem. 84(16): 2088-9 (1980).

$ClSCN^-$



Transient [1]: $ClSCN^-$, λ(max) = 390 nm, ϵ_{390} = (4700 ± 900) L mol^{-1} cm^{-1} [2]

System: aqueous solution of 3.8 mol L^{-1} Cl^- and 5×10^{-5} mol L^{-1} SCN^-

$ClSCN^-$

Reference: M. Schoeneshoefer, Int. J. Radiat. Phys. Chem. 1: 505-13 (1969)

Transient generation: pulse radiolysis [3] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay = 20 μs [4]

Transient formation:

$$OH + Cl^- \rightleftharpoons ClOH^-$$

$$ClOH^- \rightleftharpoons Cl + OH^-$$

$$Cl^- + Cl \rightleftharpoons Cl_2^-$$

$$Cl_2^- + SCN^- \rightarrow 2Cl^- + SCN$$

$$SCN + SCN^- \rightarrow (SCN)_2^-$$

$$(SCN)_2^- + Cl^- \rightleftharpoons SCN^- + ClSCN^-, \ K = 3.3 \times 10^{-3}$$

Footnotes:

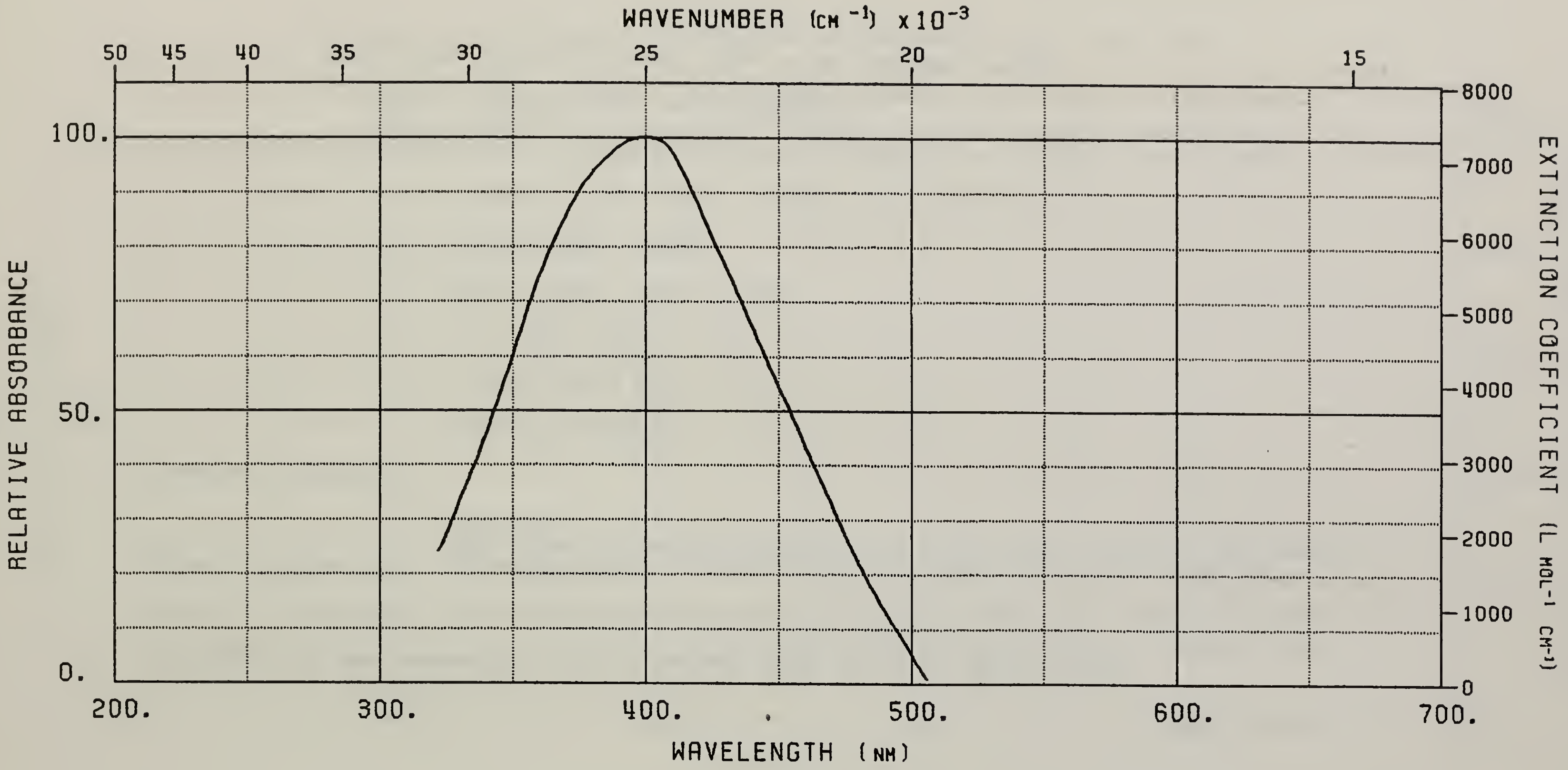
[1] Obtained from a mixed spectrum due to $(SCN)_2^-$ and $ClSCN^-$. Since $ClSCN^-$ absorbes very little at 520 nm, the contribution of $(SCN)_2^-$ which does absorb at 520 nm could be determined.

[2] Based on ϵ_{520} = 5300 L mol^{-1} cm^{-1} for $(SCN)_2^-$.

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[4] Under the experimental conditions the half-life of Cl_2^- was 5 μs.

$BrSCN^-$



Transient [1]: $BrSCN^-$, $\lambda(max)$ = 400 nm, ϵ_{400} = 7300 L mol^{-1} cm^{-1} [2]

System: aqueous solution of 2×10^{-2} mol L^{-1} Br^- and 1×10^{-4} mol L^{-1} SCN^-

$BrSCN^-$

Reference: M. Schoeneshoefer and A. Henglein, Ber. Bunsenges. Phys. Chem. 73(3): 289-93 (1969)

Transient generation: pulse radiolysis [3] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay greater than 10 μs [4]

Transient formation:

$$Br^- + OH \rightleftharpoons BrOH^-$$

$$BrOH^- \rightleftharpoons Br + OH^-$$

$$Br + Br^- \rightleftharpoons Br_2^-$$

$$Br_2^- + SCN^- \rightarrow 2Br^- + SCN$$

$$SCN + SCN^- \rightleftharpoons (SCN)_2^-$$

$$Br_2^- + SCN^- \rightleftharpoons BrSCN^- + Br^-, \; K = 10^3$$

$$SCN + Br^- \rightleftharpoons SCNBr^-$$

$$(SCN)_2^- + Br^- \rightleftharpoons SCN^- + BrSCN^-, \; K = 9.1 \times 10^{-3}$$

Footnotes:

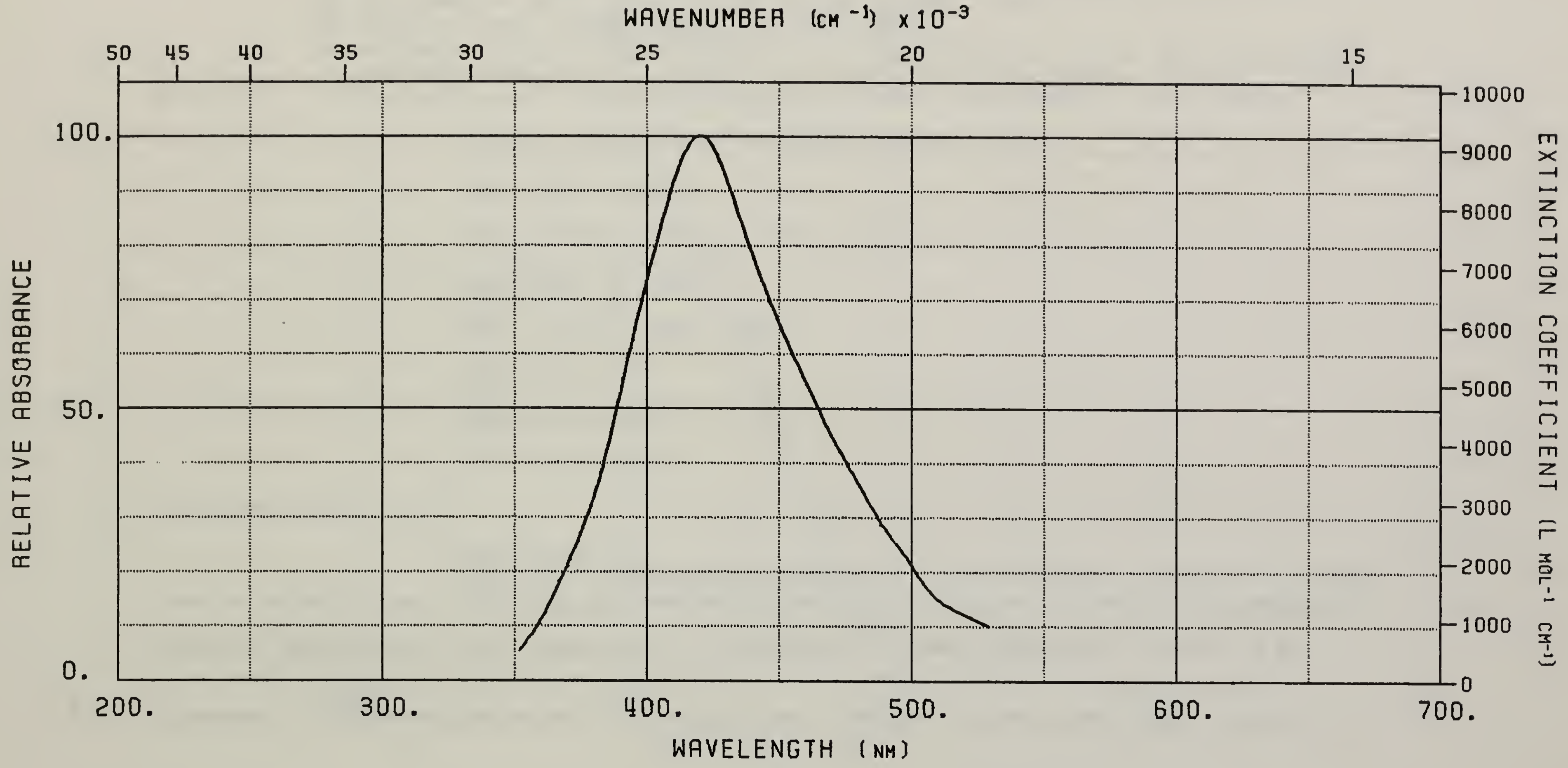
[1] Obtained from a mixed spectrum due to $(SCN)_2^-$ and $BrSCN^-$. Since $BrSCN^-$ absorbes very little at 520 nm, the contribution of $(SCN)_2^-$ which does absorb at 520 nm could be determined.

[2] Based on ϵ_{520} = 5300 L mol^{-1} cm^{-1} for $(SCN)_2^-$.

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[4] For ratios of $[Br^-]/[SCN^-] \leq 200$, it was found that there was very little Br_2^- present.

$ISCN^-$



Transient [1,2]: $ISCN^-$, $\lambda(max) = 420$ nm, $\epsilon_{420} = 9200$ L mol^{-1} cm^{-1}

System: aqueous solution of 1 mol L^{-1} SCN^- and 10^{-4} mol L^{-1} I^-, saturated with N_2O

$ISCN^-$

Reference: M. Schoeneshoefer and A. Henglein, Ber. Bunsenges. Phys. Chem. 74(4): 393-8 (1970)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 20 μs

Transient formation:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + SCN^- \rightleftharpoons HOSCN^-$$

$$HOSCN^- \rightleftharpoons OH^- + SCN$$

$$SCN + SCN^- \rightleftharpoons (SCN)_2^-$$

$$(SCN)_2^- + I^- \rightleftharpoons ISCN^- + SCN^-,\ K = 400$$

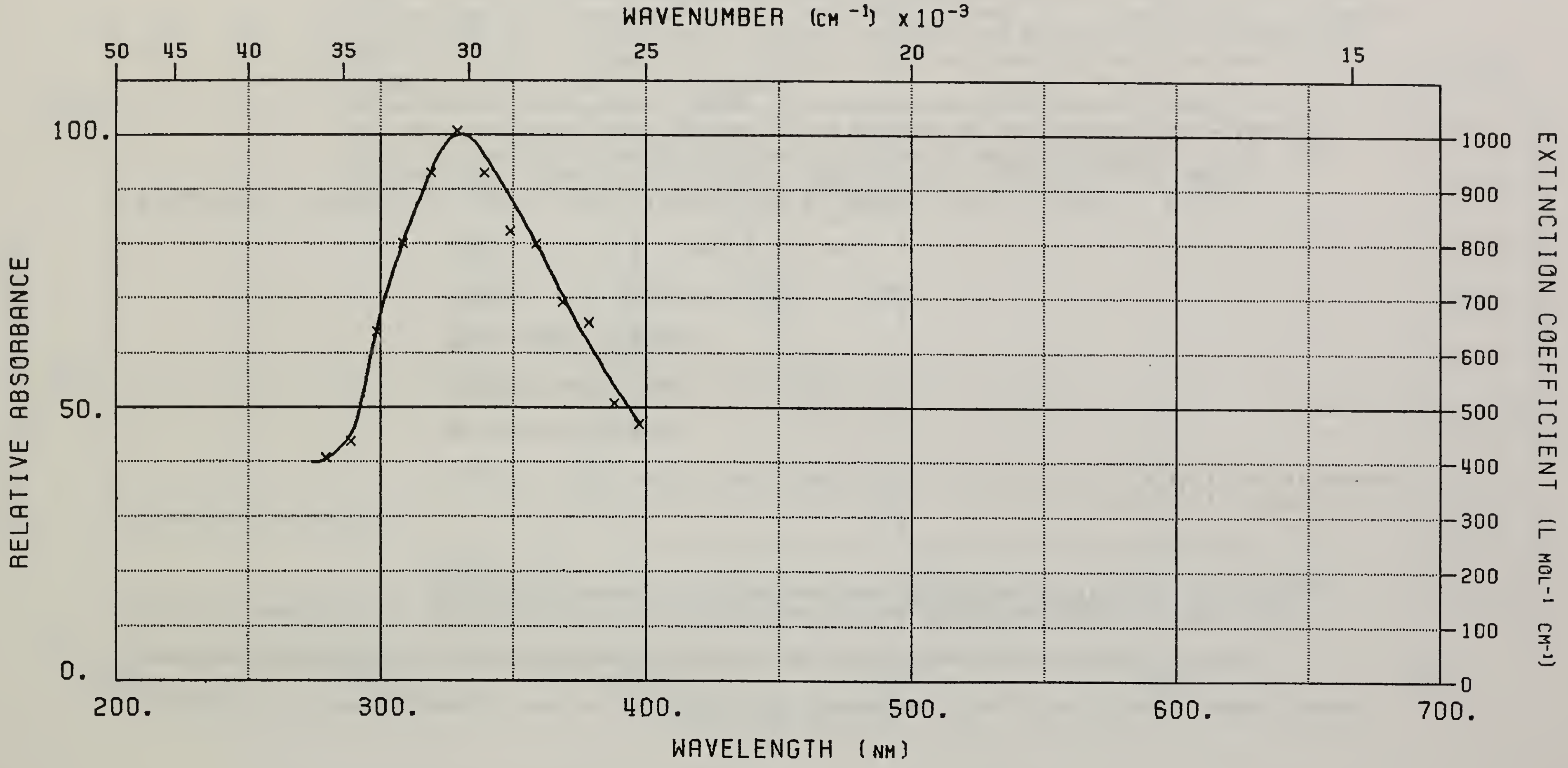
$$ISCN^- + I^- \rightleftharpoons I_2^- + SCN^-,\ K = 55$$

Footnotes:

[1] Obtained from a mixed spectrum due to $(SCN)_2^-$, I_2^- and $ISCN^-$. Since I_2^- and $ISCN^-$ absorb very little at 550 nm, the contribution of $(SCN)_2^-$ could be subtracted using the dose and yield of OH radicals of G = 5.5. I_2^- does not contribute much because it is present in small quantities under the experimental conditions. Using the measured rate constants, $[(SCN)_2^-] : [ISCN^-] : [I_2^-] = 25 : 1 : 0.0055$.

[2] Since the ratio of $[(SCN)_2^-] : [ISCN^-] = 25$, the shape of the spectrum is not very well established. Another spectrum was given in the reference for the initial conditions $[SCN^-] = 0.1$ mol L^{-1} and $[I^-] = 10^{-4}$ mol L^{-1}. However, in this case much more absorption was evident near 350 nm. Since the ratio of $[(SCN)_2^-] : [ISCN^-] : [I_2^-] = 2.5 : 1 : 0.055$ in this latter experiment, the additional absorption at 350 nm may have been due to I_2^- instead of $ISCN^-$.

$(NCO)_2^-$



Transient: $(NCO)_2^-$, $\lambda(max)$ = 330 nm, ϵ_{330} = (1000 ± 100) L mol^{-1} cm^{-1} [1]

System: aqueous solution of 10^{-1} mol L^{-1} NCO^-, N_2O-saturated, pH = 5.0 ± 0.2 [2]

$(NCO)_2^-$

Reference: J.G. Leopold and M. Faraggi, J. Phys. Chem. 81(8): 803-6 (1977)

Transient generation: pulse radiolysis [3]; energy 5 MeV; dosimetry-electron coil [4]

Spectral acquisition: 150 W xenon lamp; Bausch & Lomb high-intensity monochromator; 1P28A or R136 PMT; Type 556 Tektronix double beam oscilloscope with Polaroid camera

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$NCO^- + OH \rightarrow HNCOO^-$$

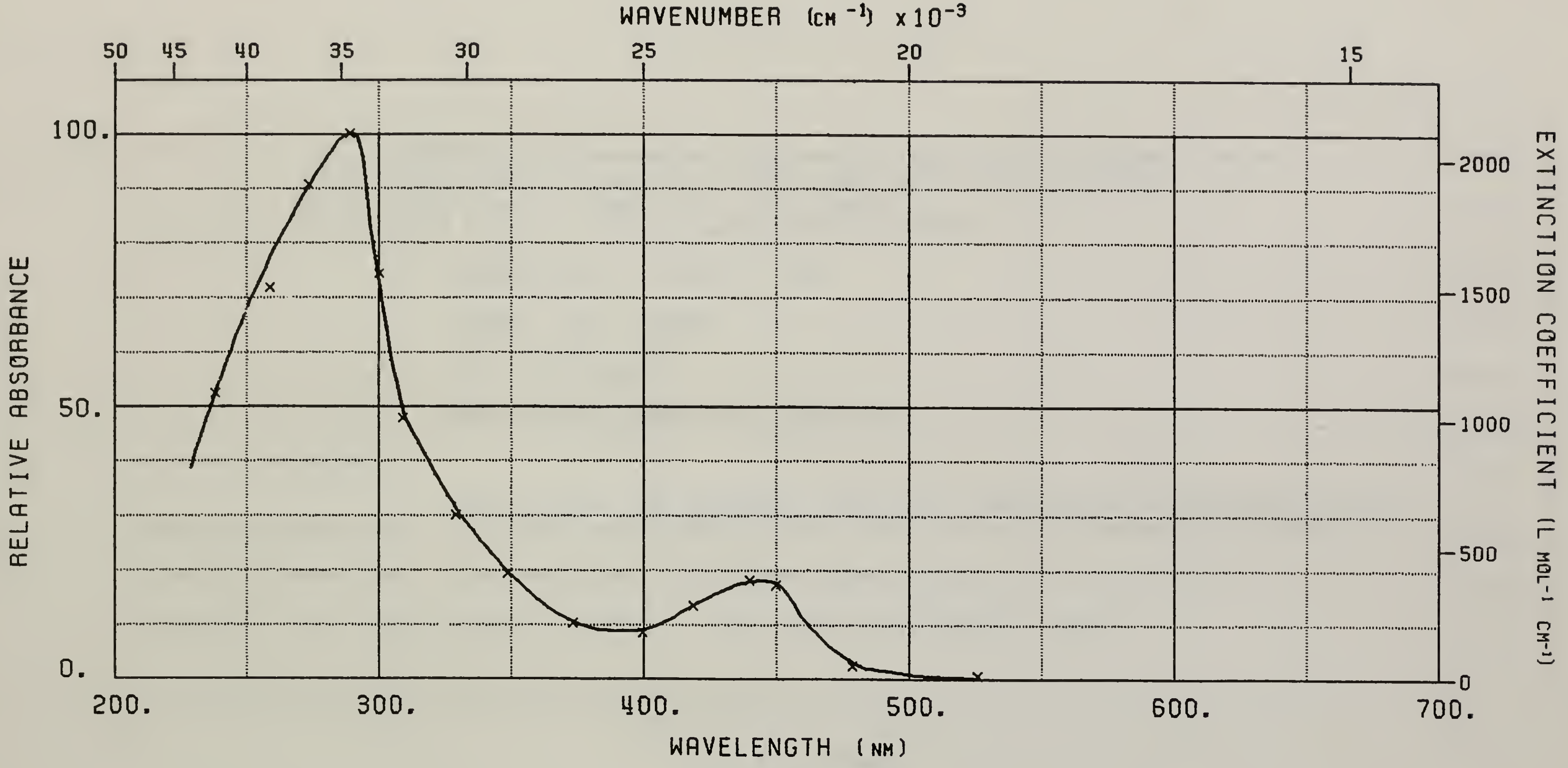
$$HNCOO^- + H^+ \rightleftharpoons HNCOOH$$

$$HNCOOH + NCO^- \rightleftharpoons (NCO)_2^- + H_2O$$

Footnotes:

[1] Based on $G(OH) = 5.6$ for N_2O-saturated solutions.
[2] Dose was such that $[OH] = 9.7 \times 10^{-6}$ mol L^{-1}.
[3] M. Faraggi and Y. Tendler, J. Chem. Phys. 56(7): 3287-93 (1972).
[4] Dosimetry used N_2O saturated solutions of 10^{-2} mol L^{-1} $Fe(CN)_6{}^{4-}$, using $G(Fe(CN)_6{}^{3-}) = 6.1$

$(CN)_2^-$



Transient: $(CN)_2^-$, cyanogen radical ion, $\lambda(max) = 290$ nm, $\epsilon_{290} = 2100$ L mol^{-1} cm^{-1}, and $\lambda(max) = 440$ nm, $\epsilon_{440} = 360$ L mol^{-1} cm^{-1} [1]

System: aqueous solution of 3.7×10^{-4} mol L^{-1} $(CN)_2$, He-purged, at natural pH ≈ 6

$(CN)_2^-$

Reference: I.C. Draganic, Z.D. Draganic, and R.A. Holroyd, J. Phys. Chem. 75(5): 608-12 (1971)

Transient generation: pulse radiolysis using Febetron 705 system; energy 2 MeV; pulse length < 0.1 μs; dos^ 4.72 krad/pulse; two dosimetry methods were used [2]; syringe technique

Spectral acquisition: 450 W xenon analyzing lamp with an arc booster [3]; path length 4.0 cm; high-intensity Bausch & Lomb grating monochromators; Amperex XP 1003 PMT; Tektronix 434 oscilloscope

Transient formation [4]:

$$(CN)_2 + e(aq)^- \rightarrow (CN)_2^-$$

Footnotes:

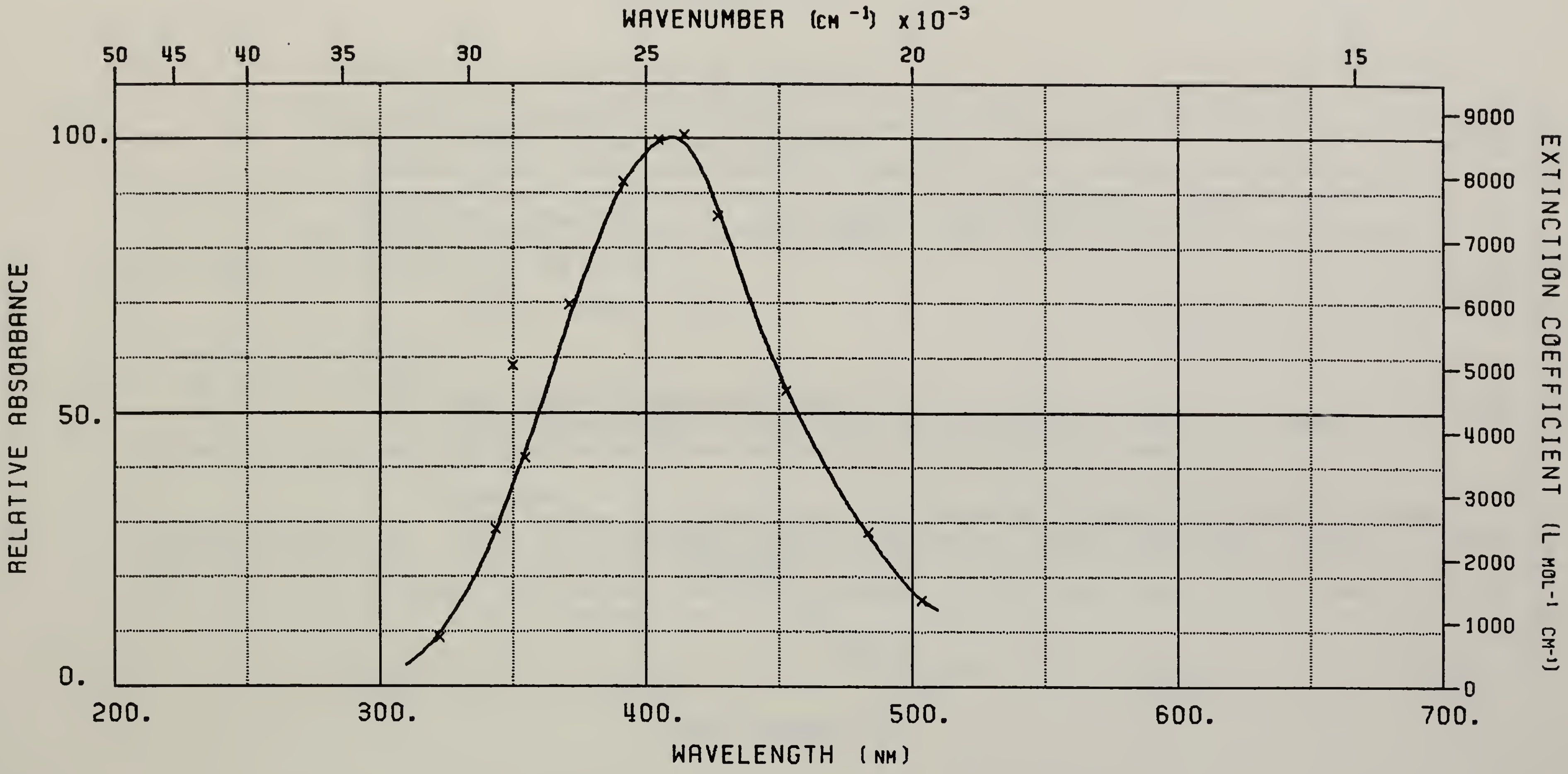
[1] Corrected for OH absorption.

[2] The first method used N_2O-saturated aqueous solutions of 0.1 mol L^{-1} thiocyanate using $\epsilon_{500} = 7600$ L mol^{-1} cm^{-1} for $(SCN)_2^-$. The second method used N_2O-saturated aqueous solutions of 10^{-3} mol L^{-1} ferrocyanide containing a small amount of air. In this system $\epsilon_{420} = 1000$ L mol^{-1} cm^{-1} for the ferricyanide formed. Both methods assumed G(product) = 5.4.

[3] Increased lamp intensity in ultraviolet by 60-fold.

[4] The reaction of $(CN)_2$ with OH was too slow ($k \leq 10^7$ L mol^{-1} s^{-1}) for the product to interfere with the spectrum.

$H_2Se_2^-$



Transient: $H_2Se_2^-$, $\lambda(max)$ = 410 nm, ϵ_{410} = 8600 L mol^{-1} cm^{-1} [1]

System: aqueous solution [2] of 10^{-3} mol L^{-1} H_2Se, Ar-saturated, pH = 3.7

$H_2Se_2^-$

Reference: M. Schoeneshoefer, W. Karmann, and A. Henglein, Int. J. Radiat. Phys. Chem. 1: 407-23 (1969)

Transient generation: pulse radiolysis, Van de Graaff generator; energy 1.6 MeV; dose rate during the pulse was 700 rad per μs; dosimetry based on SCN^- [3]

Spectral acquisition [4]: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay-immediately after pulse

Transient formation:

$$e(aq)^- + H_2Se \rightarrow HSe^- + H$$

$$H + H_2Se \rightarrow H_2 + HSe$$

$$OH + H_2Se \rightarrow H_2O + HSe$$

$$OH + HSe^- \rightarrow OH^- + HSe, \ pK_a(H_2Se) = 3.77$$

$$HSe + HSe^- \rightleftharpoons H_2Se_2^-$$

Footnotes:

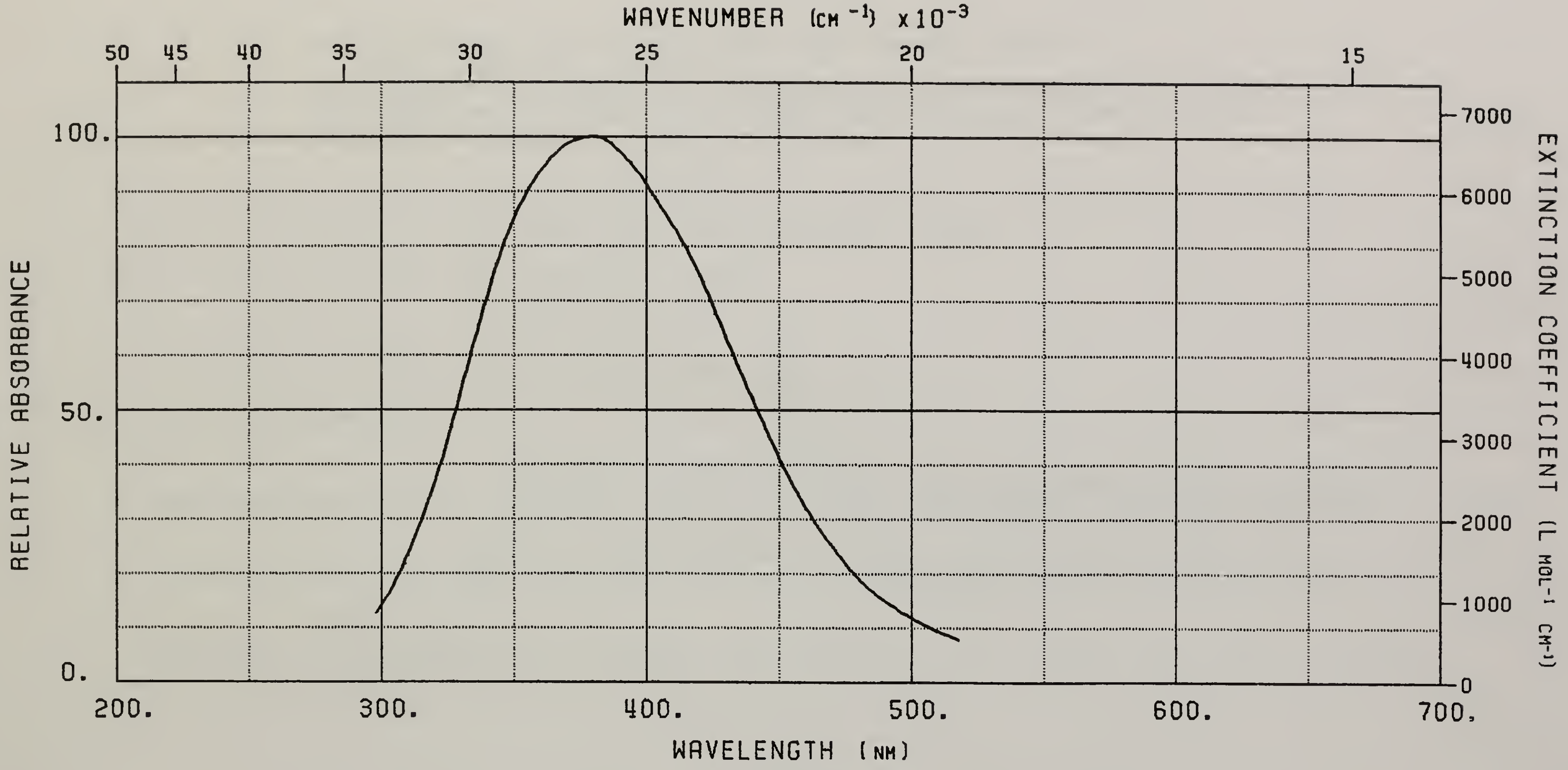
[1] Based on $G(H_2Se_2^-) = 6$.

[2] Oxygen was removed from water before H_2Se was added to make solution.

[3] Based on the measurement of SCN^- solutions under equivalent conditions, using $\epsilon_{500} = 7100$ L mol^{-1} cm^{-1}.

[4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

$(SH)_2^-$ or S_2H^{2-}



Transient [1]: $(SH)_2^-$ or S_2H^{2-}, λ(max) = 380 nm

System: aqueous solution of 10^{-3} mol L^{-1} H_2S, pH = 6.6

$(SH)_2^-$ or S_2H^{2-}

Reference: W. Karmann, G. Meissner, and A. Henglein, Z. Naturforsch. Pt. B 22(3): 273-82 (1967)

Transient generation: pulse radiolysis [2] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

Transient formation:

$e(aq)^- + H_2S \rightarrow SH^- + H$, $pK_a(H_2S) = 7$

$H + H_2S \rightarrow H_2 + HS$

$OH + H_2S \rightarrow H_2O + HS$

$HS + HS^- \rightarrow (SH)_2^-$

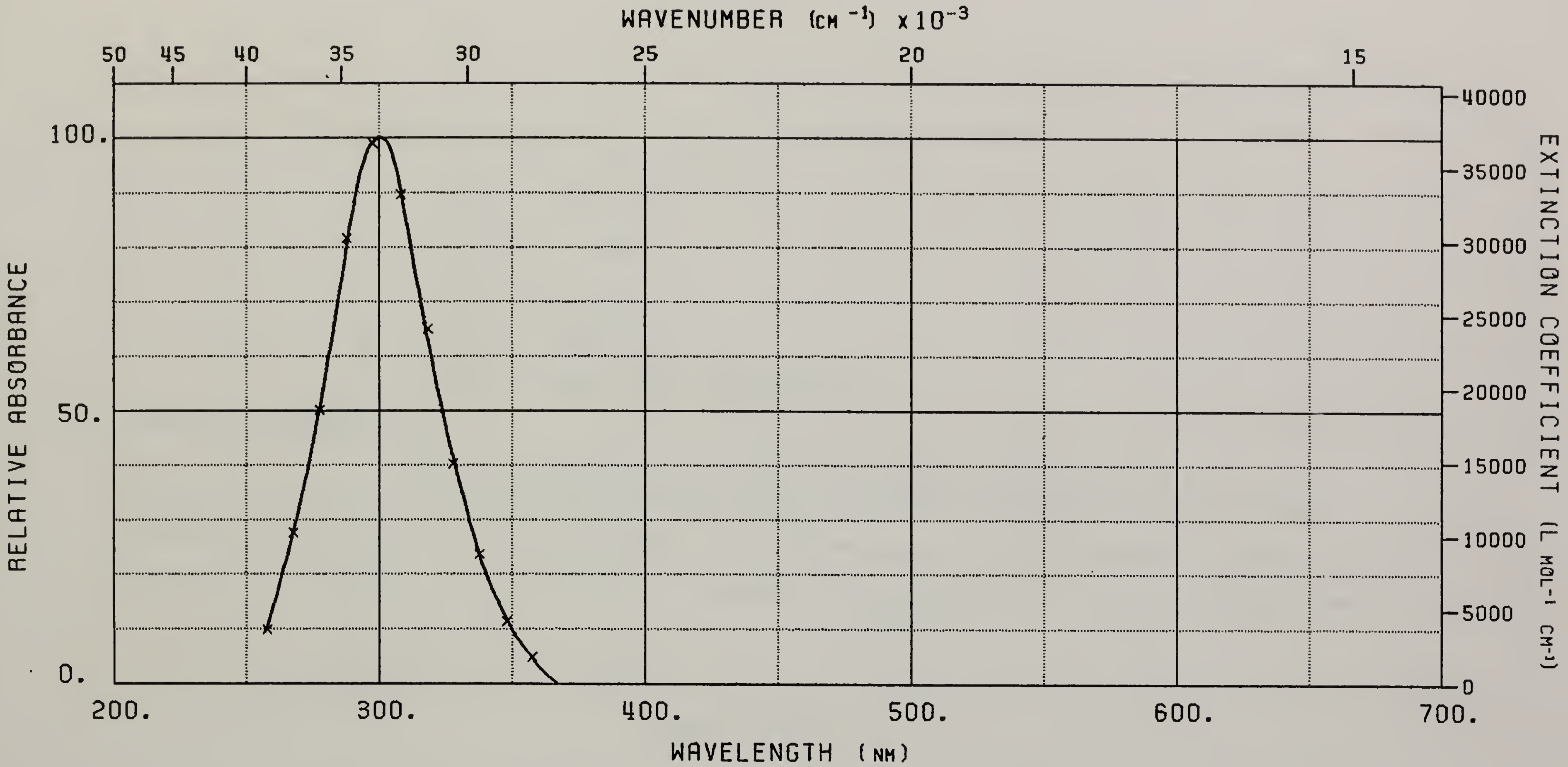
$(SH)_2^- \rightleftharpoons S_2H^{2-} + H^+$

Footnotes:

[1] Extinction coefficient based on $G = 6$.

[2] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

I_2SCN^-



Transient [1]: I_2SCN^-, $\lambda(\max) = 300$ nm, $\epsilon_{300} = 37{,}000$ L mol^{-1} cm^{-1} [2]

System: aqueous solution of 10^{-1} mol L^{-1} SCN^- and 2×10^{-4} mol L^{-1} I^-, saturated with N_2O

I_2SCN^-

Reference: M. Schoeneshoefer and A. Henglein, Ber. Bunsenges. Phys. Chem. 74(4): 393-8 (1970)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 200 μs

Transient formation :

$$I_2^- + (SCN)_2^- \rightarrow I_2SCN^- + SCN^-$$

$$I_2^- + ISCN^- \rightarrow I_2SCN^- + I^-$$

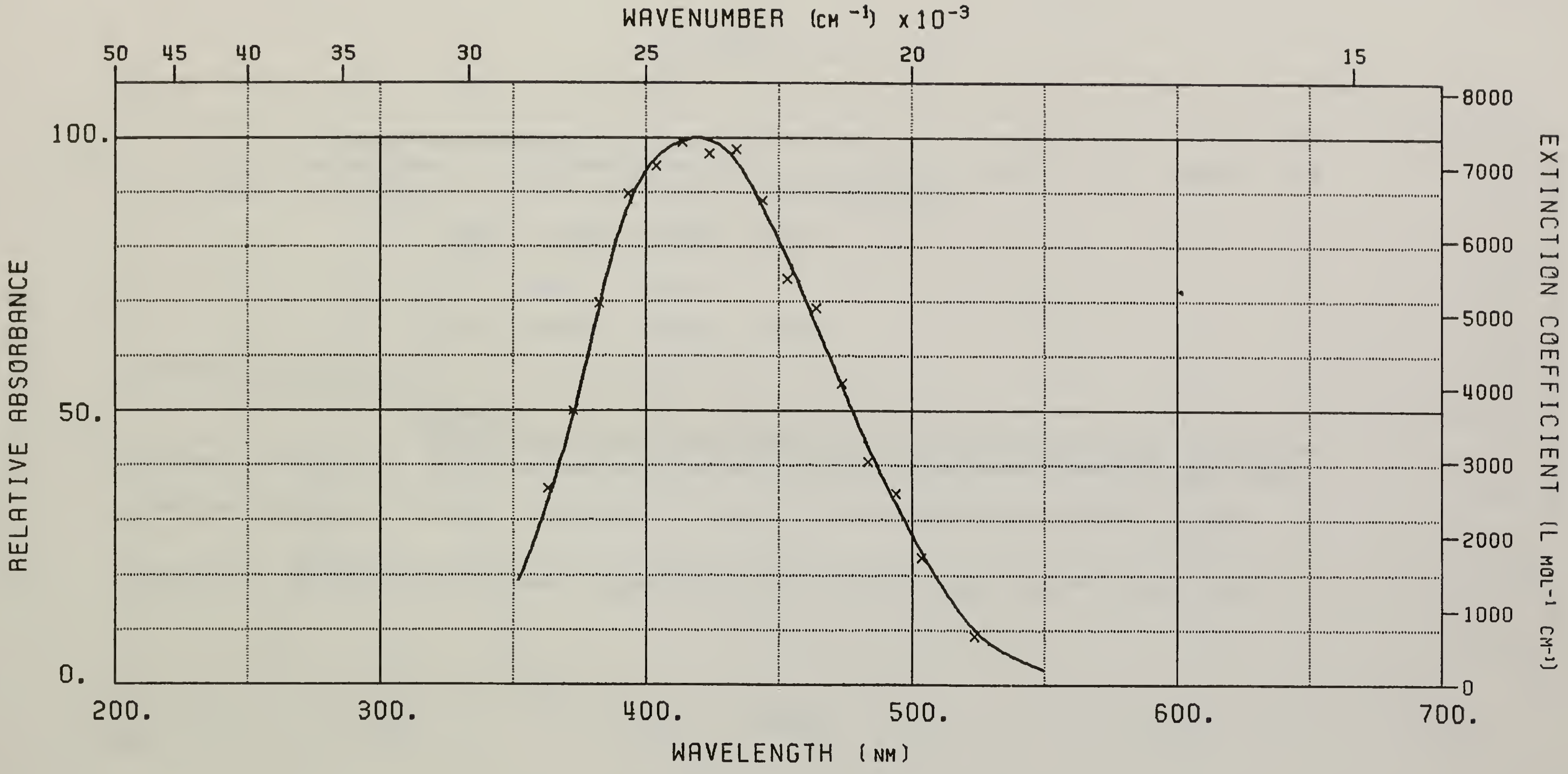
$$ISCN^- + ISCN^- \rightarrow I_2SCN^- + SCN^-$$

Footnotes:

[1] Compound is relatively stable in acid solutions.

[2] Assuming G = 2.75 and assuming G for the three complexes, I_2^-, $(SCN)_2^-$, and $ISCN^-$, was collectively 5.5.

$SCNS_2O_3{}^{2-}$



Transient [1]: $SCNS_2O_3{}^{2-}$, λ(max) = 420 nm, ϵ_{420} = 7400 L mol^{-1} cm^{-1} [2]

System: aqueous solution of 5 x 10^{-2} mol L^{-1} SCN^- and 4 x 10^{-4} mol L^{-1} $S_2O_3{}^{2-}$, saturated with N_2O [3]

$SCNS_2O_3{}^{2-}$

Reference: M. Schoeneshoefer, Ber. Bunsenges. Phys. Chem. 77(4): 257-62 (1973)

Transient generation: pulse radiolysis [4] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

Transient formation [5]:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + SCN^- \rightleftharpoons HOSCN^-$$

$$HOSCN^- \rightleftharpoons SCN + OH^-$$

$$SCN + SCN^- \rightleftharpoons (SCN)_2{}^-$$

$$(SCN)_2{}^- + S_2O_3{}^{2-} \rightleftharpoons SCNS_2O_3{}^{2-} + SCN^-, \ K = (1.6 \pm 0.4) \times 10^2$$

Footnotes:

[1] Obtained from a mixed spectrum due to $(SCN)_2{}^-$, $S_4O_6{}^{3-}$, and $SCNS_2O_3{}^{2-}$. The $SCNS_2O_3{}^{2-}$ spectrum was obtained from the experimental spectrum using a kinetic analysis.

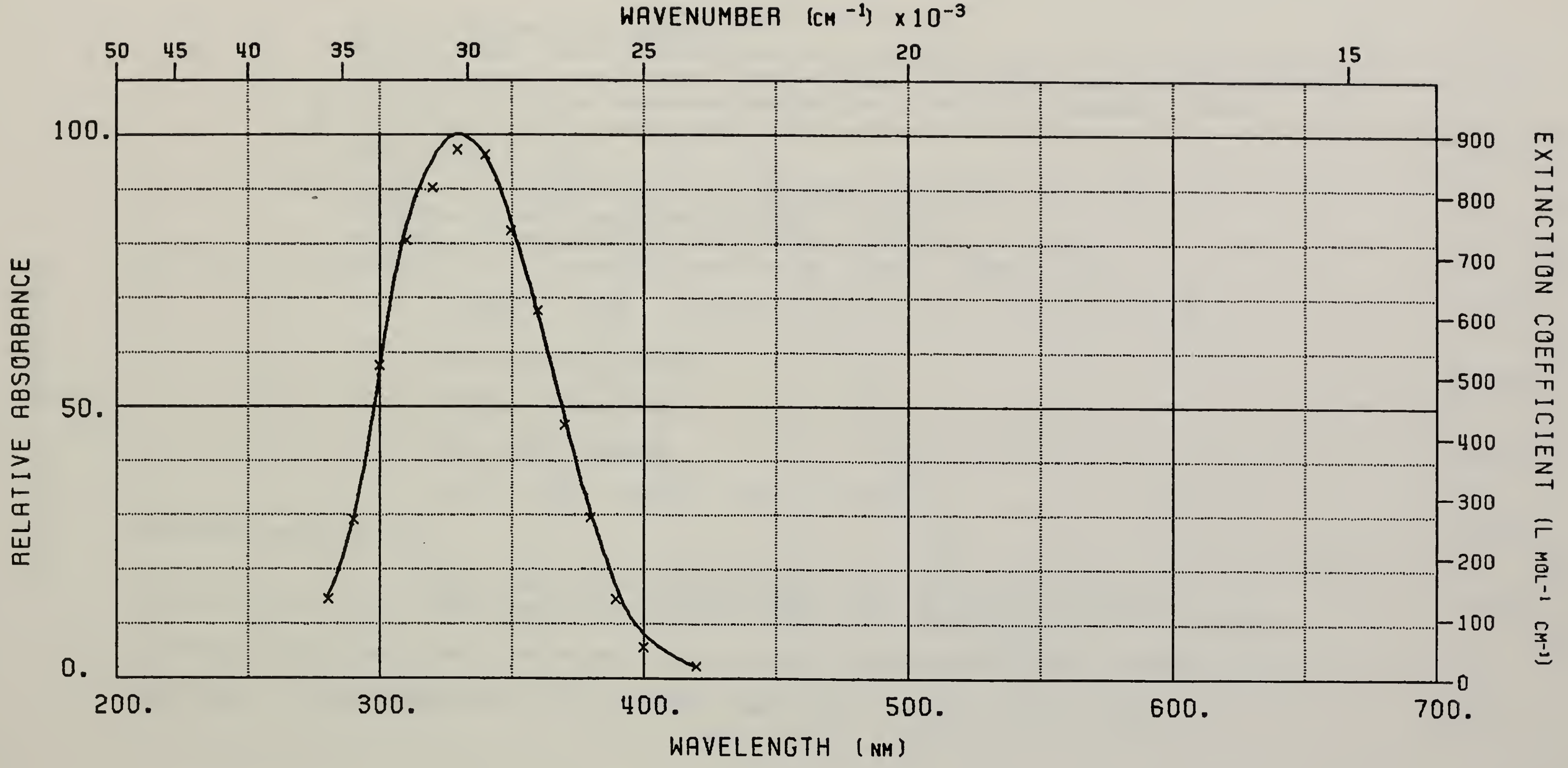
[2] Based on $\epsilon = 1600$ L mol^{-1} cm^{-1} for $S_4O_6{}^{3-}$ and 7100 L mol^{-1} cm^{-1} for the ϵ of $(SCN)_2{}^-$.

[3] G(OH) taken to be 6.

[4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[5] Shows only the most prominent pathway for formation of $SCNS_2O_3{}^{2-}$ under the experimental conditions. Several other equilibria complicate the analysis. In particular, there are two important mechanisms that lead to formation of $S_4O_6{}^{3-}$ starting from $SCNS_2O_3{}^{2-}$.

SCN



Transient [1]: SCN, λ(max) = 330 nm, ϵ_{330} = 900 L mol^{-1} cm^{-1} [2]

System: aqueous solution of 10^{-4} mol L^{-1} SCN$^-$, saturated with N_2O, natural pH

SCN

Reference: D. Behar, P.L.T. Bevan, and G. Scholes, J. Phys. Chem. 76(11): 1537-42 (1972)

Transient generation: pulse radiolysis, linear accelerator; pulse length 0.1 μs; doses 0.1 to 1.0 krad

Spectral acquisition: kinetic spectroscopy; time delay 1 μs

Transient formation [3]:

$e(aq)^- + N_2O\ (+H_2O) \rightarrow N_2 + OH + OH^-$

$OH + SCN^- \rightarrow HOSCN^-$

$HOSCN^- \rightleftharpoons SCN + OH^-$, $K = 3.2 \times 10^{-2}$ mol L^{-1}

$SCN + SCN^- \rightleftharpoons (SCN)_2^-$, $K = 2 \times 10^5$ L mol^{-1}

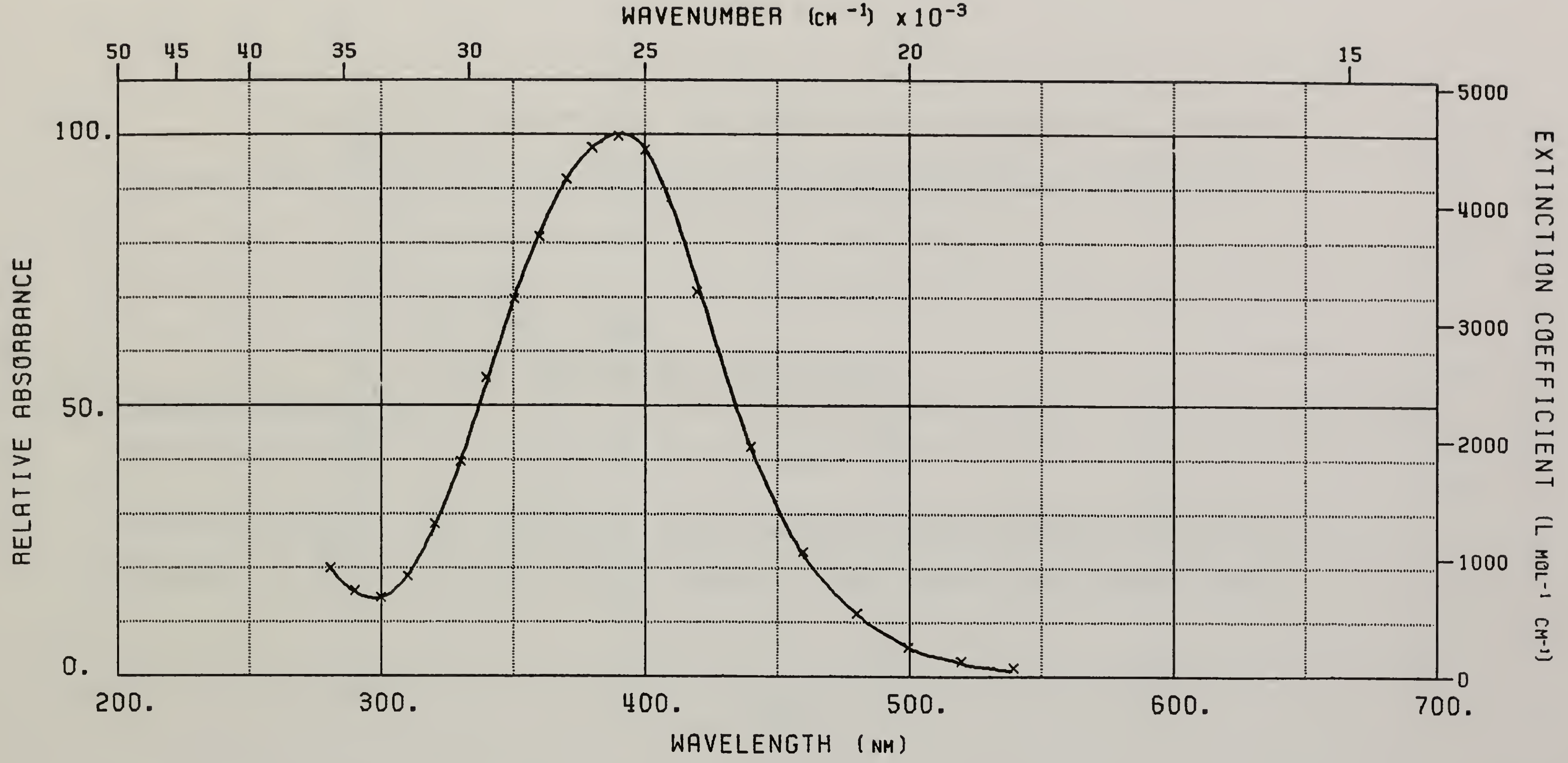
Footnotes:

[1] Obtained from a composite spectrum by subtracting $(SCN)_2^-$ contribution.

[2] Based on the kinetic analysis and the value 7600 L mol^{-1} cm^{-1} for ϵ_{475} of $(SCN)_2^-$.

[3] Mechanism involving $SCNO^{2-}$ was eliminated by considering $[OH^-]$ dependence.

$HOSCN^-$



Transient [1]: $HOSCN^-$, $\lambda(max)$ = 390 nm, ϵ_{390} = 4600 L mol^{-1} cm^{-1} [2]

System: aqueous solution of 10^{-4} mol L^{-1} SCN^- and 10^{-1} mol L^{-1} OH^-, saturated with N_2O

$HOSCN^-$

Reference: D. Behar, P.L.T. Bevan, and G. Scholes, J. Phys. Chem. 76(11): 1537-42 (1972)

Transient generation: pulse radiolysis, linear accelerator; pulse length 0.1 μs; doses 0.1 to 1.0 krad

Spectral acquisition: kinetic spectroscopy; time delay 3.5 μs

Transient formation [3]:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + OH^- \rightleftharpoons O^- + H_2O$$

$$OH + SCN^- \rightarrow HOSCN^-$$

$$O^- + SCN^- \rightarrow OSCN^{2-}$$

$$OSCN^{2-} + H_2O \rightleftharpoons HOSCN^- + OH^-$$

$$HOSCN^- + SCN^- \rightleftharpoons (SCN)_2^- + OH^-$$

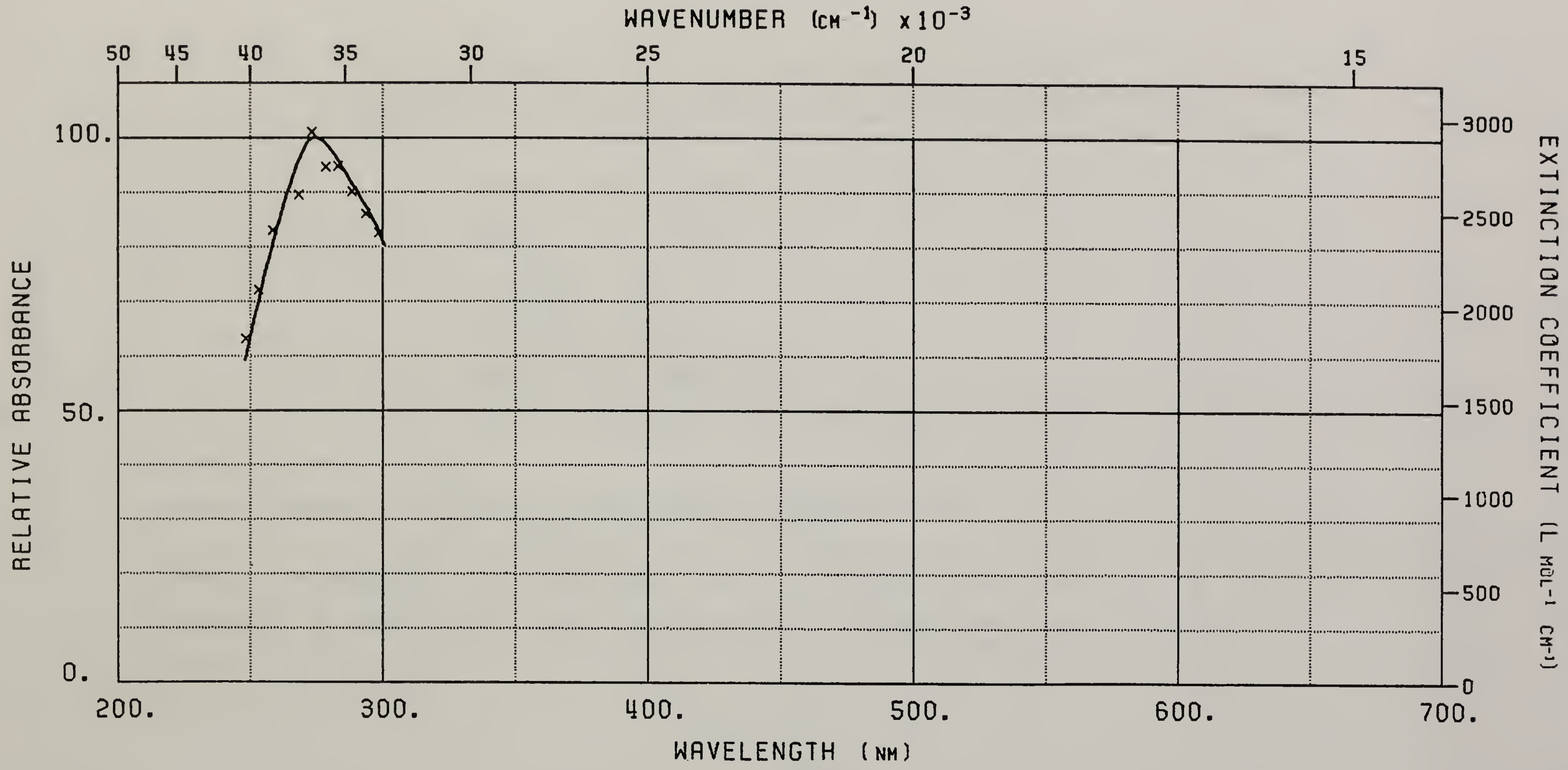
Footnotes:

[1] Obtained from a composite spectrum by subtracting $(SCN)_2^-$ contribution.

[2] Based on extinction coefficients at 390 nm and 475 nm.

[3] The transient $OSCN^{2-}$ was shown to have a neglible concentration by a study of the dependence of the spectrum on OH^- concentration.

Br



Transient [1]: Br [2], bromine atom, λ(max) = 275 nm, ε(max) = 2900 L mol^{-1} cm^{-1} [3,4]

System: aqueous solution of 2.5 x 10^{-3} mol L^{-1} Br_2 and 1.4 mol L^{-1} $HClO_4$, argon saturated before Br_2 was added

Br

Reference: A. Treinin and E. Hayon, J. Am. Chem. Soc. 97(7): 1716-21 (1975)

Transient generation: laser flash photolysis, frequency-quadrupled neodymium laser, excitation wavelength 265 nm; pulse length ≈ 15 ns; energy per pulse ≈ 2 x 10^{-2} J

Spectral acquisition: monitoring lamp was a pulsed 250 W Osram xenon lamp; monitoring beam formed a right angle to the laser beam; time delay 20 ns after pulse

Transient formation [5]:

$$Br_2 + h\nu \rightarrow 2Br$$

$$Br_3^- + h\nu \rightarrow Br + Br_2^-$$

Footnotes:

[1] Spectrum corrected for depletion of Br_2 and Br_3^- and for formation of Br_2^-.

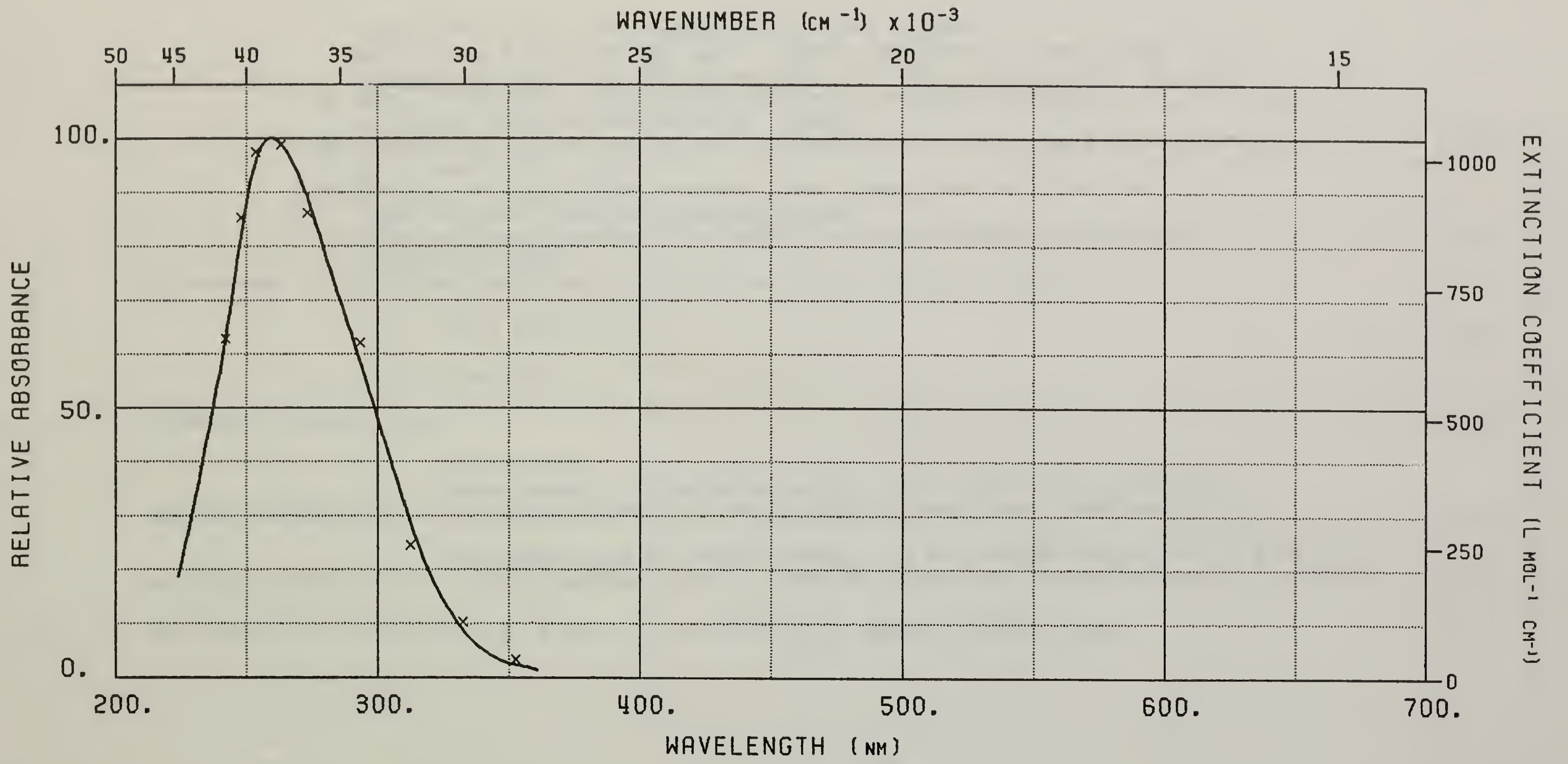
[2] Spectrum is attributed to a complex with the transition being due to an electron transfer from H_2O to Br.

[3] Extinction coefficient measured under conditions such that all Br is converted to Br_2^-.

[4] Extinction coefficient of Br_2^- is taken to be ϵ_{360} = 9900 L mol^{-1} cm^{-1}, D. Behar, private communication, 1980.

[5] Under conditions where no Br^- was added initially, authors calculated that their solutions contained 5 to 15 x 10^{-6} mol L^{-1} Br^- and 2 to 7 x 10^{-7} mol L^{-1} Br_3^-. Under experimental conditions absorbance due to Br_3^- was 0.1 to 0.2 at 265 nm.

I



Transient: I, iodine atom, $\lambda(\max)$ = 260 nm, $\epsilon(\max)$ = 1040 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 3 x 10^{-4} mol L^{-1} I_2

I

Reference: P. Fornier de Violet, R. Bonneau, and J. Joussot-Dubien, Chem. Phys. Lett. 19(2): 251-3 (1973)

Transient generation: laser flash photolysis; excitation wavelength 529 nm; pulse energy 1 J

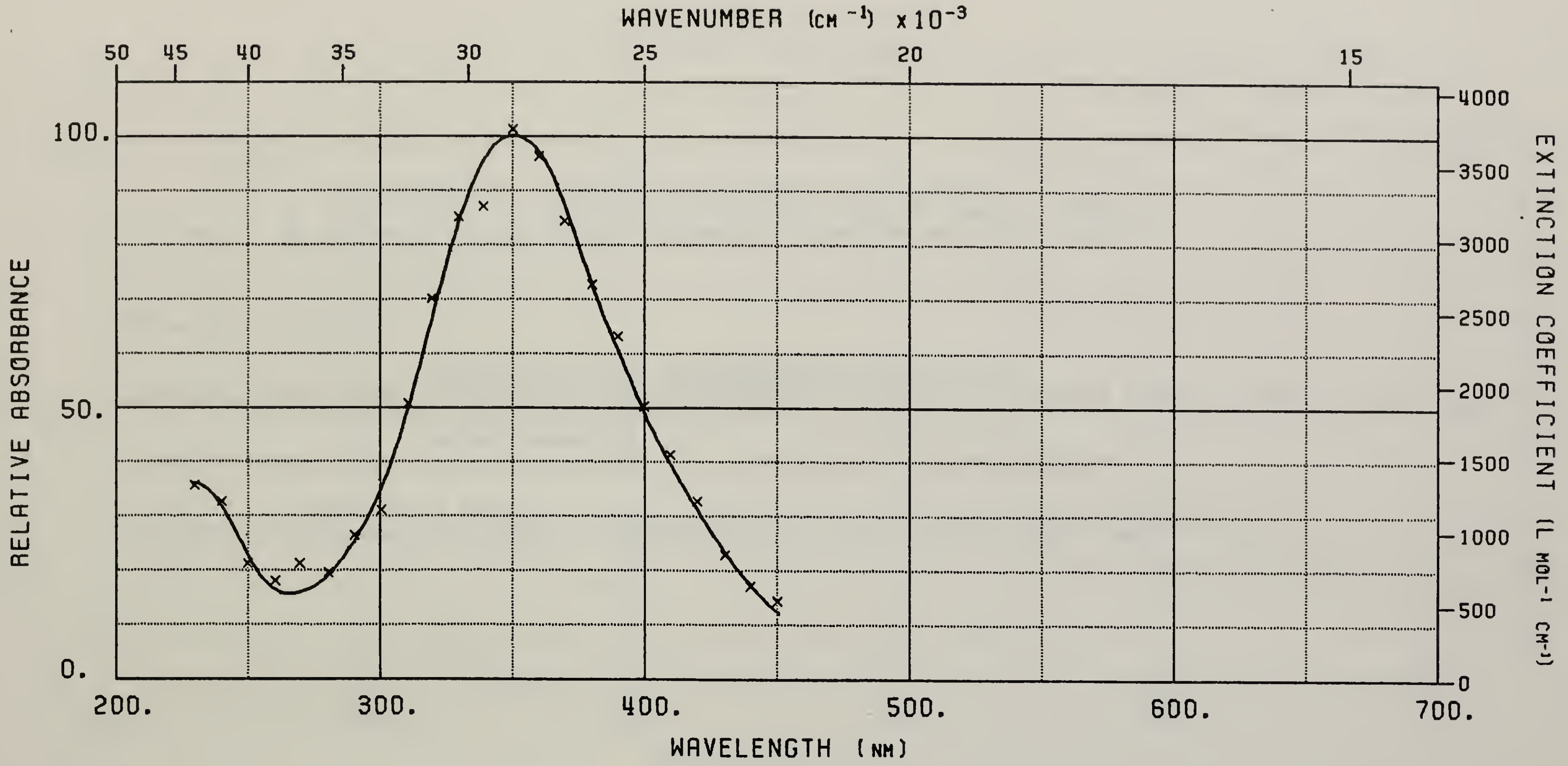
Spectral acquisition: pulsed xenon monitoring lamp; rise time of detection system < 10 ns; accuracy ≈ 0.5 % on transmission measurements

Transient formation:

$$I_2 + h\nu \rightarrow 2I$$

Footnote: [1] Extinction coefficient attributed to these authors by A. Treinin and E. Hayon, J. Am. Chem. Soc. 97(7): 1716-21 (1975). Basis for extinction coefficient measurement is not known.

$ClOH^-$



Transient [1]: $ClOH^-$, $\lambda(max)$ = 350 nm, ϵ_{350} = (3700 ± 400) L mol^{-1} cm^{-1} [2,3]

System: aqueous solution of 3 mol L^{-1} NaCl, neutral pH, N_2O or O_2 saturated [1]

$ClOH^-$

Reference: G.G. Jayson, B.J. Parsons, and A.J. Swallow, J. Chem. Soc., Faraday Trans. 1 69: 1597-607 (1973)

Transient generation: pulse radiolysis, electron linear accelerator; dose per pulse 1.63 x 10^3 rad; dosimetry-secondary emission chamber [4]

Spectral acquisition: two Bausch & Lomb high-intensity monochromators used in series to reduce scattered light

Transient formation:

$$OH + Cl^- \rightleftharpoons ClOH^-; \ K = (0.70 \pm 0.13) \text{ L mol}^{-1}$$

Footnotes:

[1] The resulting spectrum was obtained from the spectra obtained from N_2O-saturated and from O_2-saturated solutions. The absorption in O_2-saturated solutions was thought to be due to both $ClOH^-$ and Cl_2^-. The Cl_2^- was thought to be formed in the spurs by hole scavenging with Cl^- or by $ClOH^- + H^+ \rightleftharpoons H_2O + Cl$ and $Cl + Cl^- \rightleftharpoons Cl_2^-$. The N_2O-saturated solutions had these reactions in addition to the extra $ClOH^-$ formed by OH formed from

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH^- + OH$$

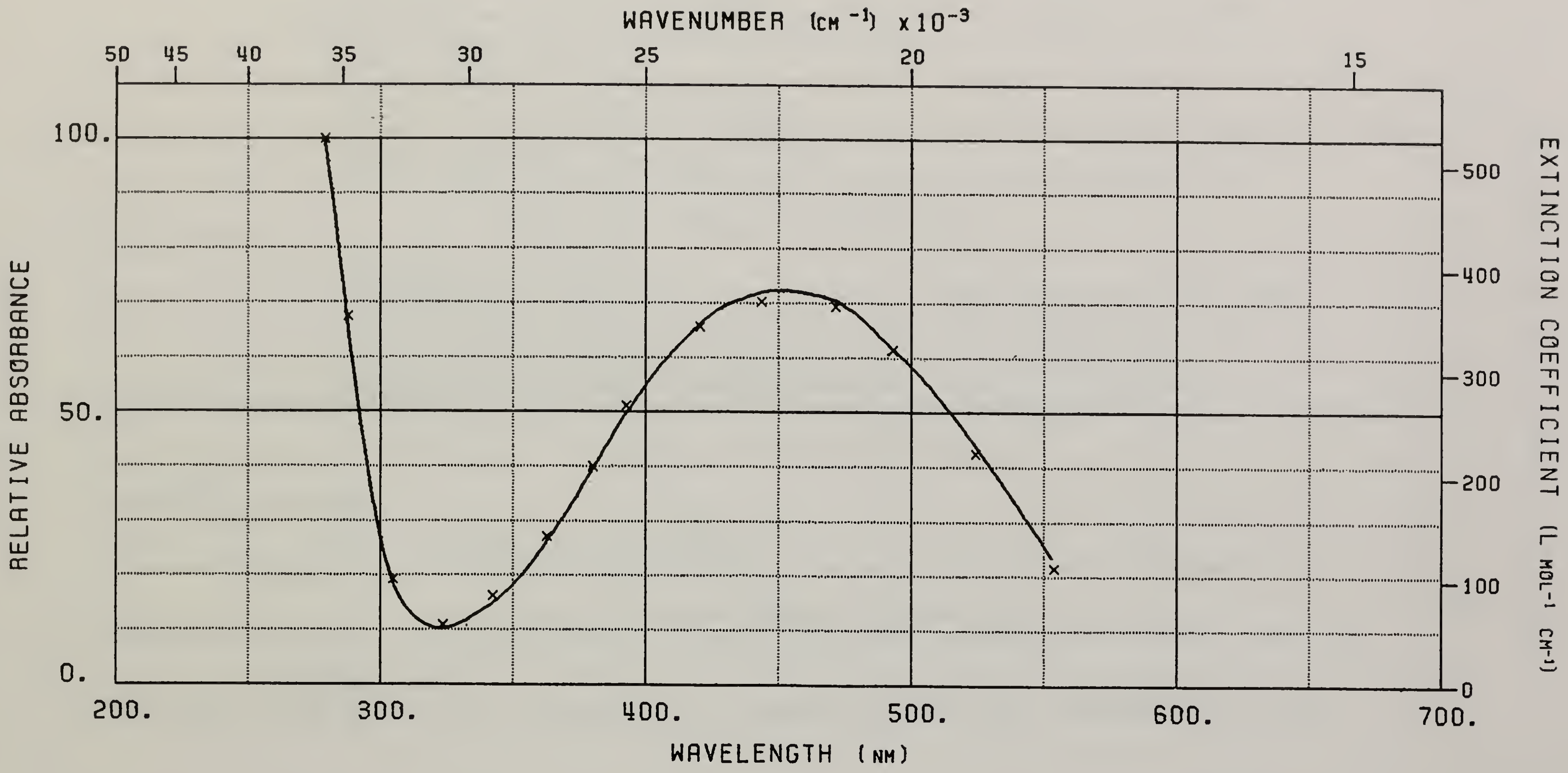
Spectra from O_2-saturated solutions were corrected for O_2^- absorption, using $\epsilon_{240} \approx 1720$ L mol^{-1} cm^{-1} for O_2^-.

[2] Assumed excess yield of OH in N_2O solutions was $G(e(aq)^-) = 2.75$ for OH formed from N_2O reaction with hydrated electron.

[3] A more recent report gave a value for $\epsilon(\max)$ of $ClOH^-$ that was much lower, $\epsilon(\max) = 1200$ L mol^{-1} cm^{-1}.
R.W. Fessenden, private communication, 1980.

[4] Calibrated by aqueous potassium thiocyanate taking $G((SCN)_2^-) = 2.9$ and $\epsilon_{600}((SCN)_2^-) = 7100$ L mol^{-1} cm^{-1}.

Se^-



Transient: Se^-, $\lambda(max)$ = 450 nm, ϵ_{450} = 380 L mol^{-1} cm^{-1} [1], 2k = (4.6 ± 1.5) x 10^9 L mol^{-1} s^{-1}

System: aqueous solution [2] of HSe^-, N_2O-saturated, pH = 11

Se^-

Reference: M. Schoeneshoefer, W. Karmann, and A. Henglein, Int. J. Radiat. Phys. Chem. 1: 407-23 (1969)

Transient generation: pulse radiolysis, Van de Graaff generator; energy 1.6 MeV; dose rate during the pulse was 700 rad per μs; dosimetry based on SCN^- [3]

Spectral acquisition [4]: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 20 μs

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + HSe^- \rightarrow H_2O + Se^-, \ pK_a(H_2Se) = 3.77$$

$$H + HSe^- \rightarrow H_2 + Se^-$$

Footnotes:

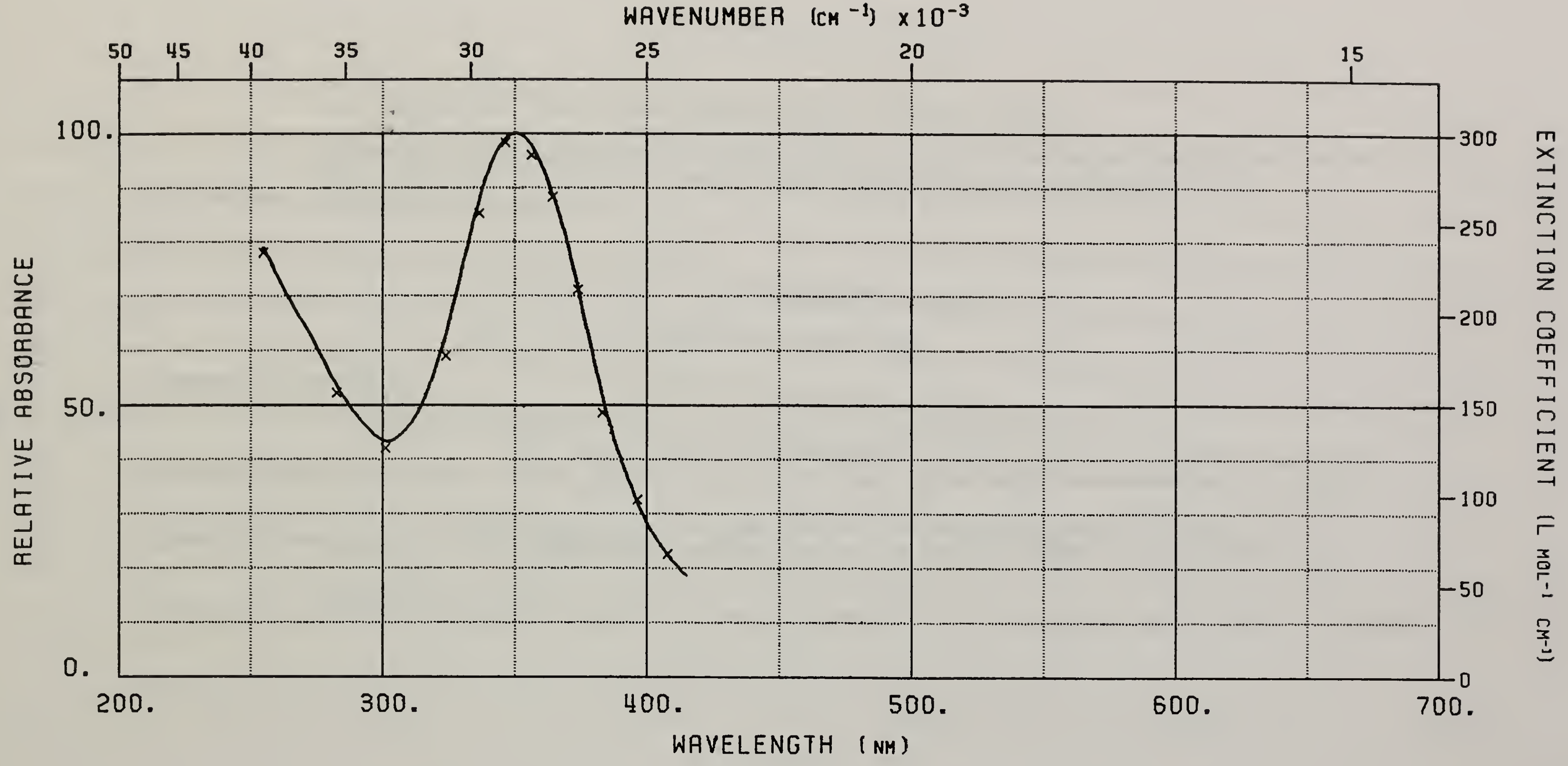
[1] Based on $G(OH) = 6$.

[2] Oxygen was removed from water before H_2Se was added to make solution.

[3] Based on the measurement of SCN^- solutions under equivalent conditions, using $\epsilon_{500} = 7100 \ L \ mol^{-1} \ cm^{-1}$.

[4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

HSe



Transient: HSe, λ(max) = 350 nm, ϵ_{350} = 300 L mol^{-1} cm^{-1} [1], 2k = (8.1 ± 2.0) x 10^{9} L mol^{-1} s^{-1}

System: aqueous solution [2] of H_2Se, N_2O-saturated, pH = 0.8

HSe

Reference: M. Schoeneshoefer, W. Karmann, and A. Henglein, Int. J. Radiat. Phys. Chem. 1: **407-23** (1969)

Transient generation: pulse radiolysis, Van de Graaff generator; energy 1.6 MeV; dose rate during the pulse was 700 rad per μs; dosimetry based on SCN^- [3]

Spectral acquisition [4]: Osram 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 5 μs after pulse

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + H_2Se \rightarrow HSe + H_2O, \ pK_a(H_2Se) = 3.77$$

$$H + H_2Se \rightarrow HSe + H_2$$

Footnotes:

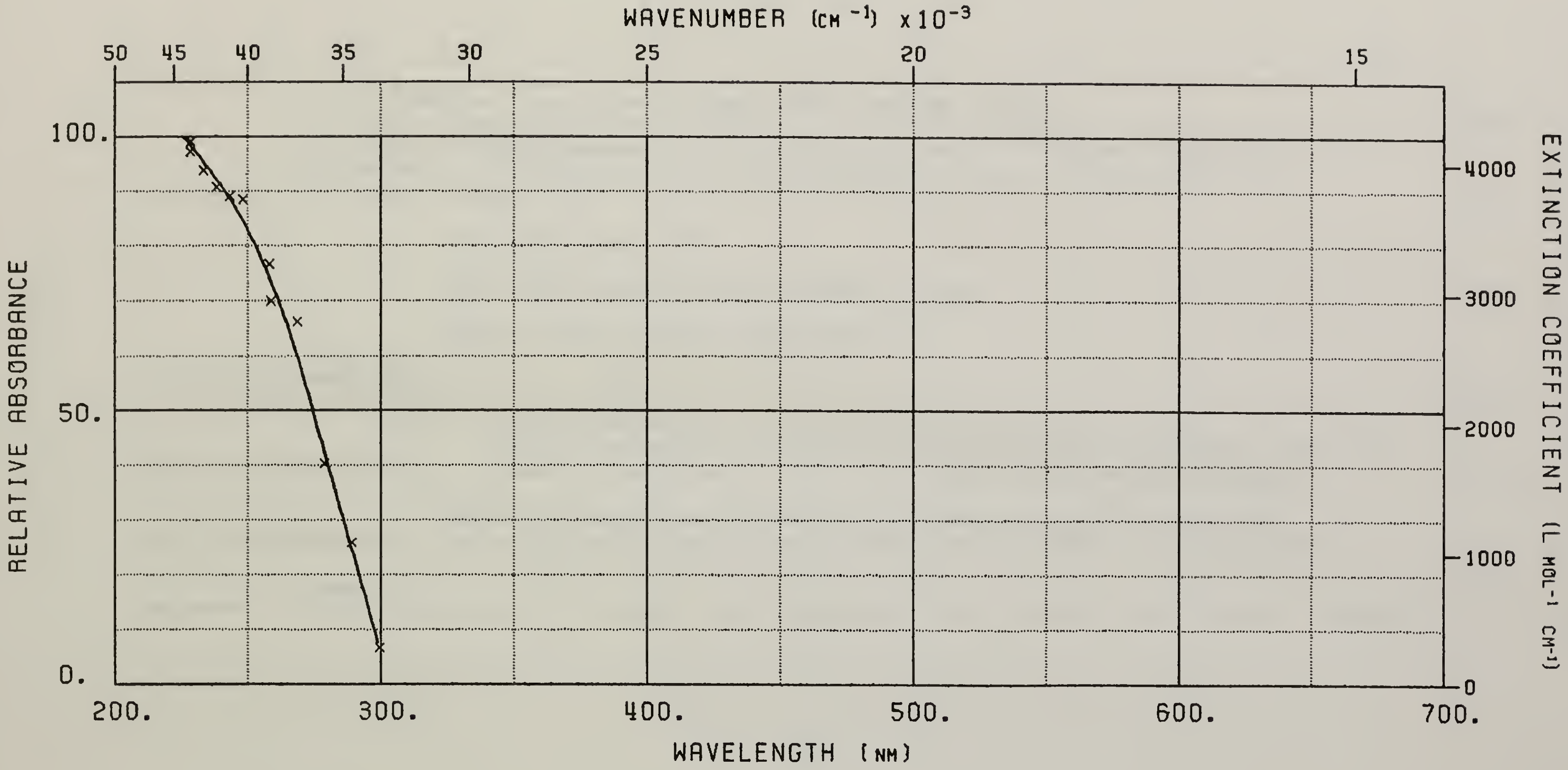
[1] Based on G(OH) = 6.

[2] Oxygen was removed from water before H_2Se was added to make solution.

[3] Based on the measurement of SCN^- solutions under equivalent conditions, using $\epsilon_{500} = 7100 \text{ L mol}^{-1} \text{ cm}^{-1}$.

[4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

PO_3^{2-}



Transient: PO_3^{2-}, phosphite radical anion, ϵ_{250} = 3500 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 2 x 10^{-3} mol L^{-1} phosphorous acid, saturated with N_2O, pH 9

PO_3^{2-}

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV; dose rate during pulse was 700 rad per μs

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 QB PMT

Transient formation:

$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$

$OH + H_2PO_3^- \rightarrow HPO_3^- + H_2O$

$H + H_2PO_3^- \rightarrow HPO_3^- + H_2$

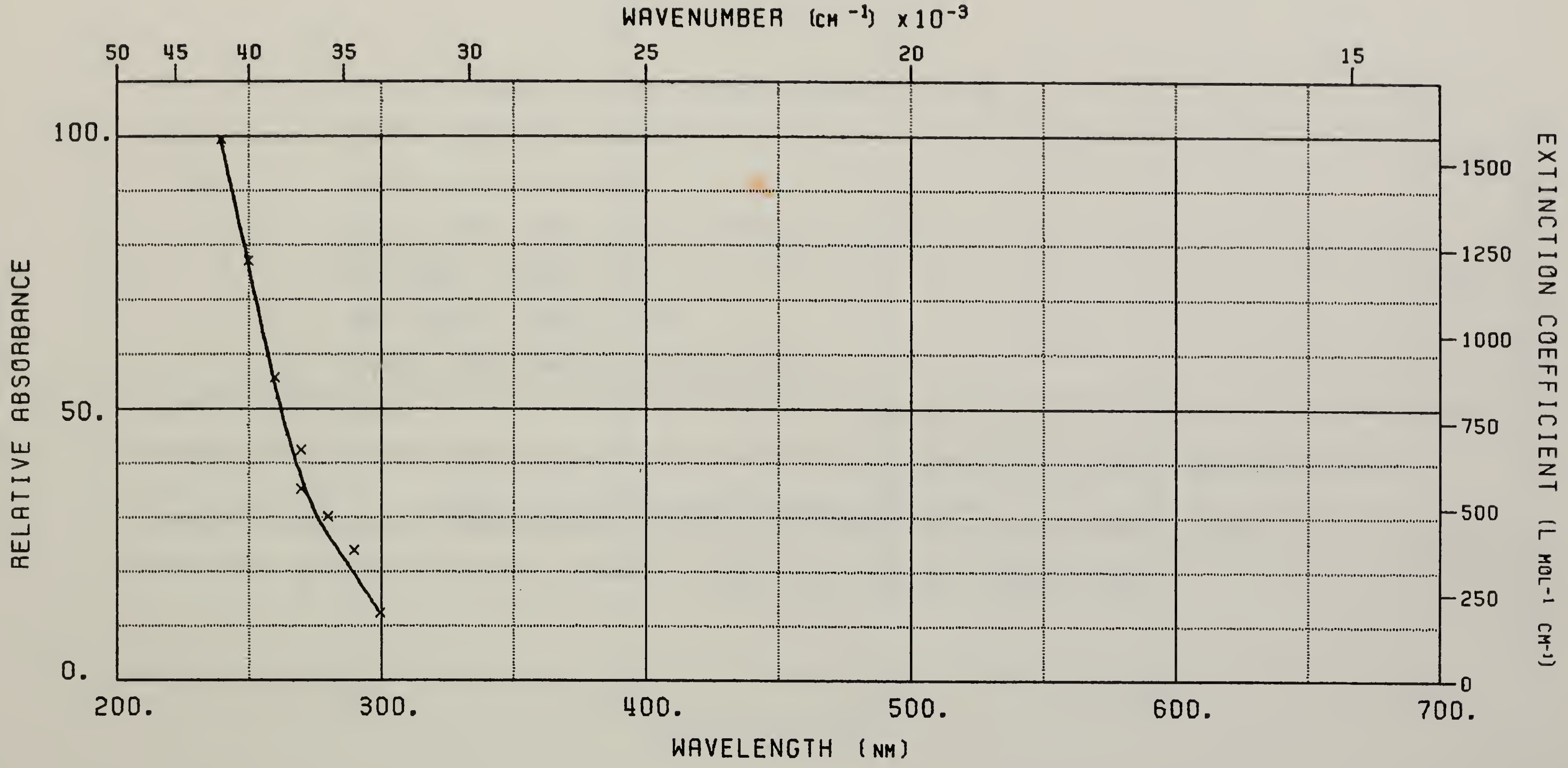
$HPO_3^- + OH^- \rightarrow H_2O + PO_3^{2-}$, $pK_a(HPO_3^-) = 5.75$

$HPO_3^{2-} + H \rightarrow H_2 + PO_3^{2-}$

$HPO_3^{2-} + OH \rightarrow H_2O + PO_3^{2-}$

Footnote: [1] Assuming $G(PO_3^{2-}) = G(OH) + G(H) + G(e(aq)^-) = 6.2$

HPO_3^-



Transient: HPO_3^-, protonated phosphite radical anion, ϵ_{250} = 1200 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 2 x 10^{-3} mol L^{-1} phosphorous acid, saturated with N_2O, pH 4

HPO_3^-

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV; dose rate during pulse was 700 rad per μs

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 QB PMT

Transient formation:

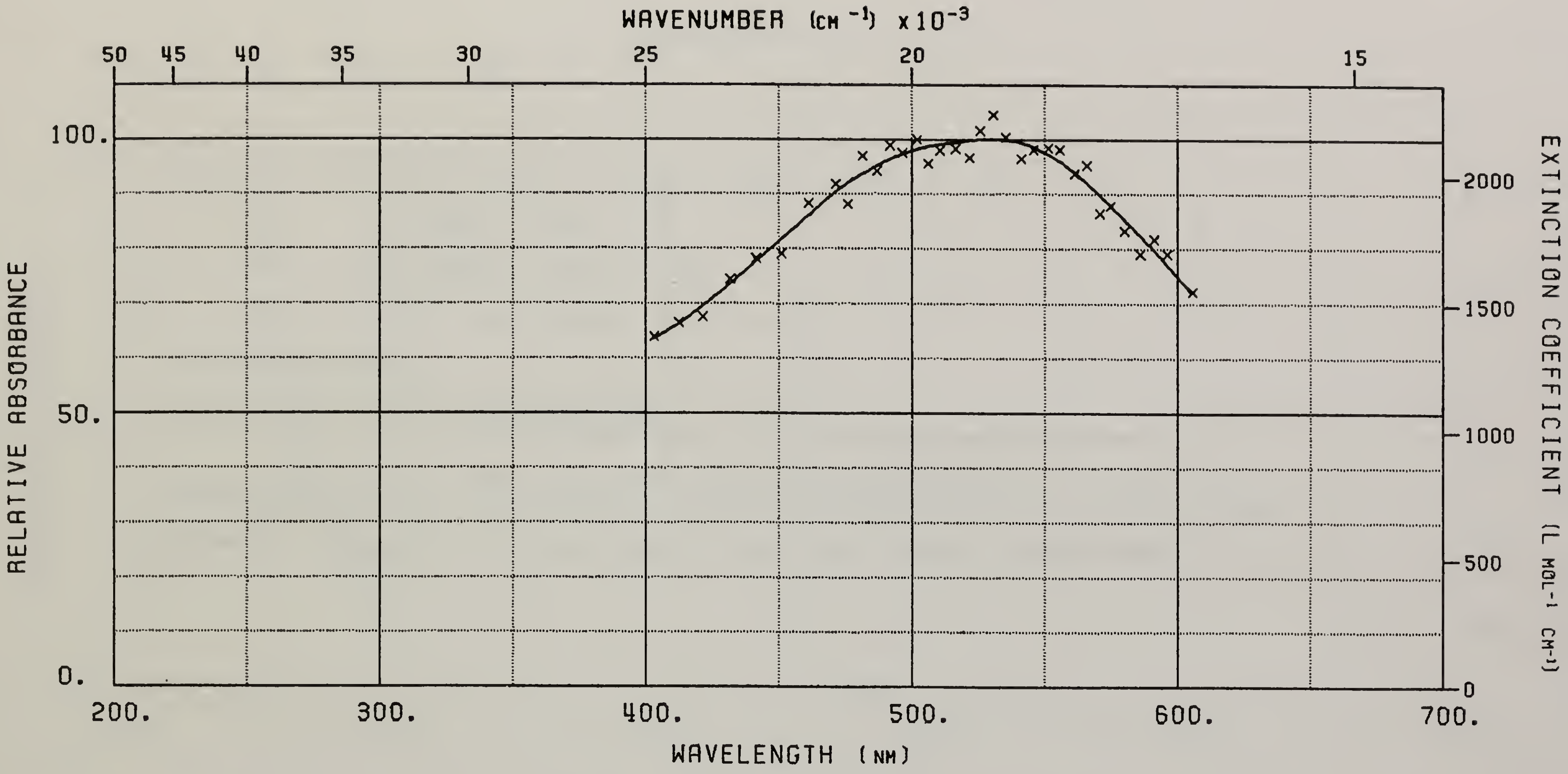
$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$

$OH + H_2PO_3^- \rightarrow HPO_3^- + H_2O$

$H + H_2PO_3^- \rightarrow HPO_3^- + H_2$

Footnote: [1] Assuming $G(HPO_3^-) = G(OH) + G(H) + G(e(aq)^-) = 6.2$

PO_4^{2-}



Transient [1]: PO_4^{2-}, $\lambda(max) = 530$ nm, $\epsilon_{530} = 2150$ L mol^{-1} cm^{-1}

System: aqueous solution of 2.5×10^{-2} mol L^{-1} peroxodiphosphate at pH 11

PO_4^{2-}

Reference: P. Maruthamuthu and P. Neta, J. Phys. Chem. 82(6): 710-13 (1978)

Transient generation: ARCO LP-7 linear accelerator; pulse length 5 ns; dosimetry thiocyanate

Spectral acquisition: Bausch & Lomb monochromator 0.5 m; photomultiplier signals digitized by Biomation 8100 recorder; signal averaging with PDP-8 computer; time delay 2-10 μs after pulse-formation was complete after this delay

Transient formation:

$$P_2O_8^{4-} + e(aq)^- \rightarrow PO_4^{3-} + PO_4^{2-}$$

$$HPO_4^- + OH^- \rightleftharpoons PO_4^{2-} + H_2O, \; pK_a(HPO_4^-) = 8.9$$

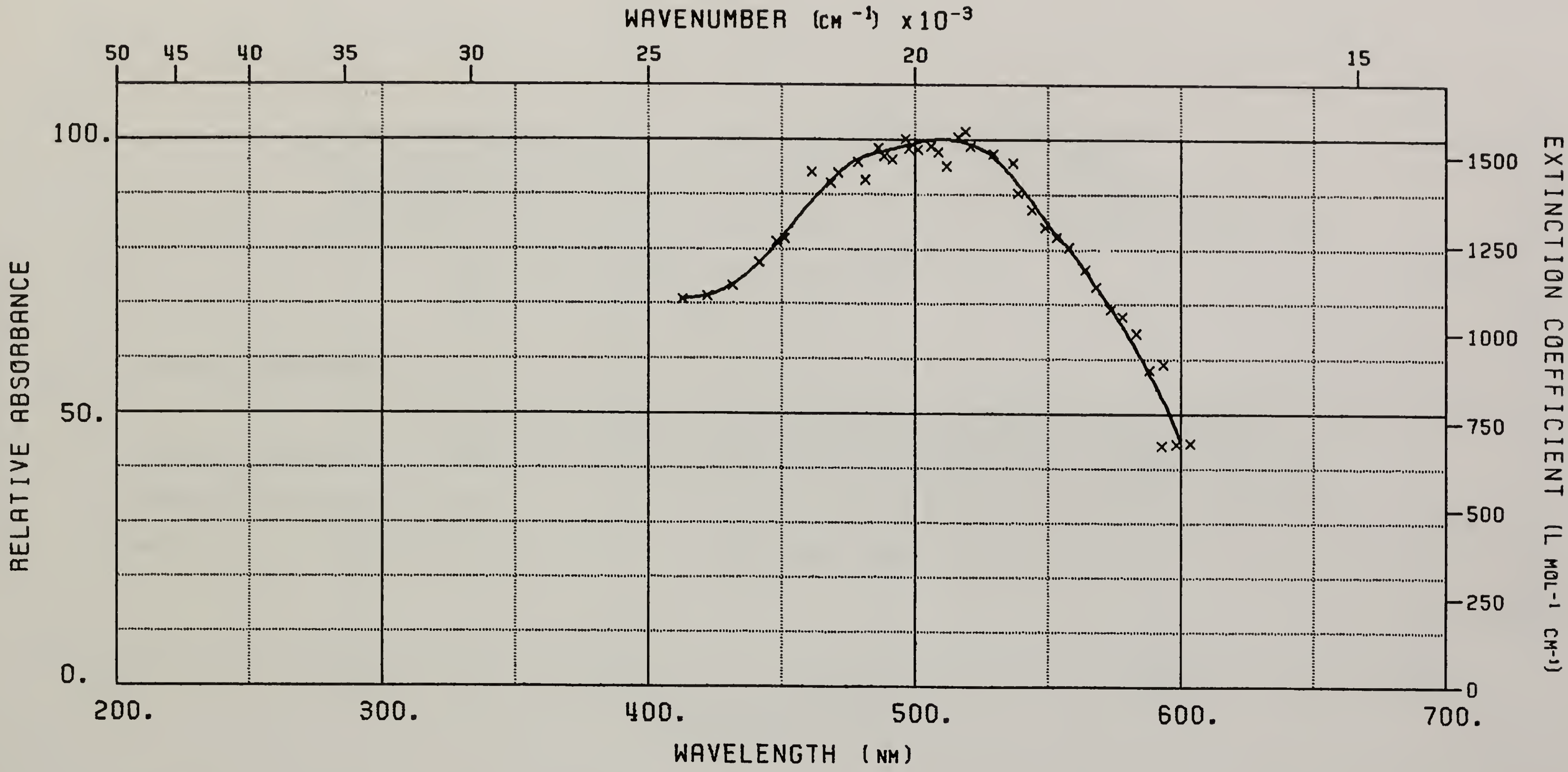
Footnotes:

[1] In other works where spectra were taken at shorter wavelengths, another peak was observed in the 300-400 nm region. For examples see references in footnotes 2 and 3.

[2] G. Levey and E.J. Hart, J. Phys. Chem. 79(16): 1642-6 (1975).

[3] E.D. Black and E. Hayon, J. Phys. Chem. 74(17): 3199-203 (1970).

HPO_4^-



Transient [1]: HPO_4^-, λ(max) = 510 nm, ϵ_{510} = 1550 L mol^{-1} cm^{-1}

System: aqueous solution of 2.5 x 10^{-2} mol L^{-1} $HP_2O_8^{3-}$ at pH 7

HPO_4^-

Reference: P. Maruthamuthu and P. Neta, J. Phys. Chem. 82(6): 710-13 (1978)

Transient generation: ARCO LP-7 linear accelerator; pulse length 5 ns; dosimetry thiocyanate

Spectral acquisition: Bausch & Lomb monochromator 0.5 m; photomultiplier signals digitized by Biomation 8100 recorder; signal averaging with PDP-8 computer; time delay 2-10 μs after pulse-formation was complete after this delay.

Transient formation [3]:

$$HP_2O_8^{3-} + e(aq)^- \rightarrow PO_4^{3-} + HPO_4^-$$

$$\rightarrow HPO_4^{2-} + PO_4^{2-}$$

$$PO_4^{2-} + H^+ \rightleftharpoons HPO_4^-,\ pK_a(HPO_4^-) = 8.9$$

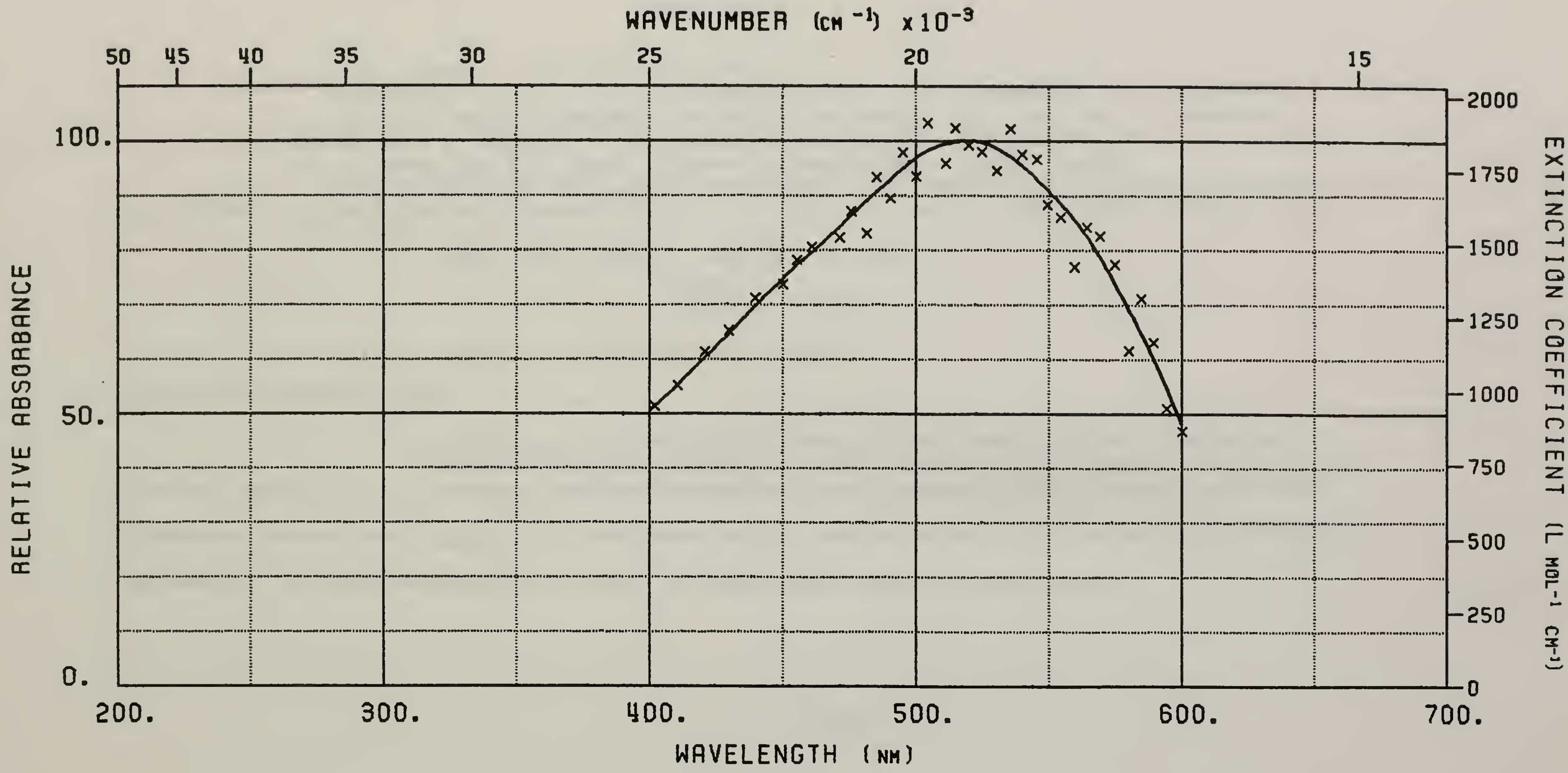
Footnotes:

[1] In other works where spectra were taken at shorter wavelengths, another peak was observed in the 300-400 nm region. For example see reference in footnote [2].

[2] G. Levey and E.J. Hart, J. Phys. Chem. 79(16): 1642-6 (1975).

[3] At pH = 7, $HP_2O_8^{3-}$ is in equilibrium with $P_2O_8^{4-}$ which is about 18% of total peroxophosphate concentration, see p. 392, Topics in Phosphorus Chemistry, Vol. 7 edited by E.J. Griffith and M. Grayson. I.I. Creaser and J.O. Edwards, "Peroxophosphates".

H_2PO_4



Transient [1]: H_2PO_4, λ(max) = 520 nm, ϵ_{520} = 1850 L mol^{-1} cm^{-1}

System: aqueous solution of 2.5 x 10^{-2} mol L^{-1} $H_2P_2O_8{}^{2-}$ ions at pH 4

H_2PO_4

Reference: P. Maruthamuthu and P. Neta, J. Phys. Chem. 82(6): 710-13 (1978)

Transient generation: ARCO LP-7 linear accelerator; pulse length 5 ns; dosimetry thiocyanate

Spectral acquisition: Bausch & Lomb monochromator 0.5 m; photomultiplier signals digitized by Biomation 8100 recorder; signal averaging with PDP-8 computer; spectrum extrapolated to time zero.

Transient formation:

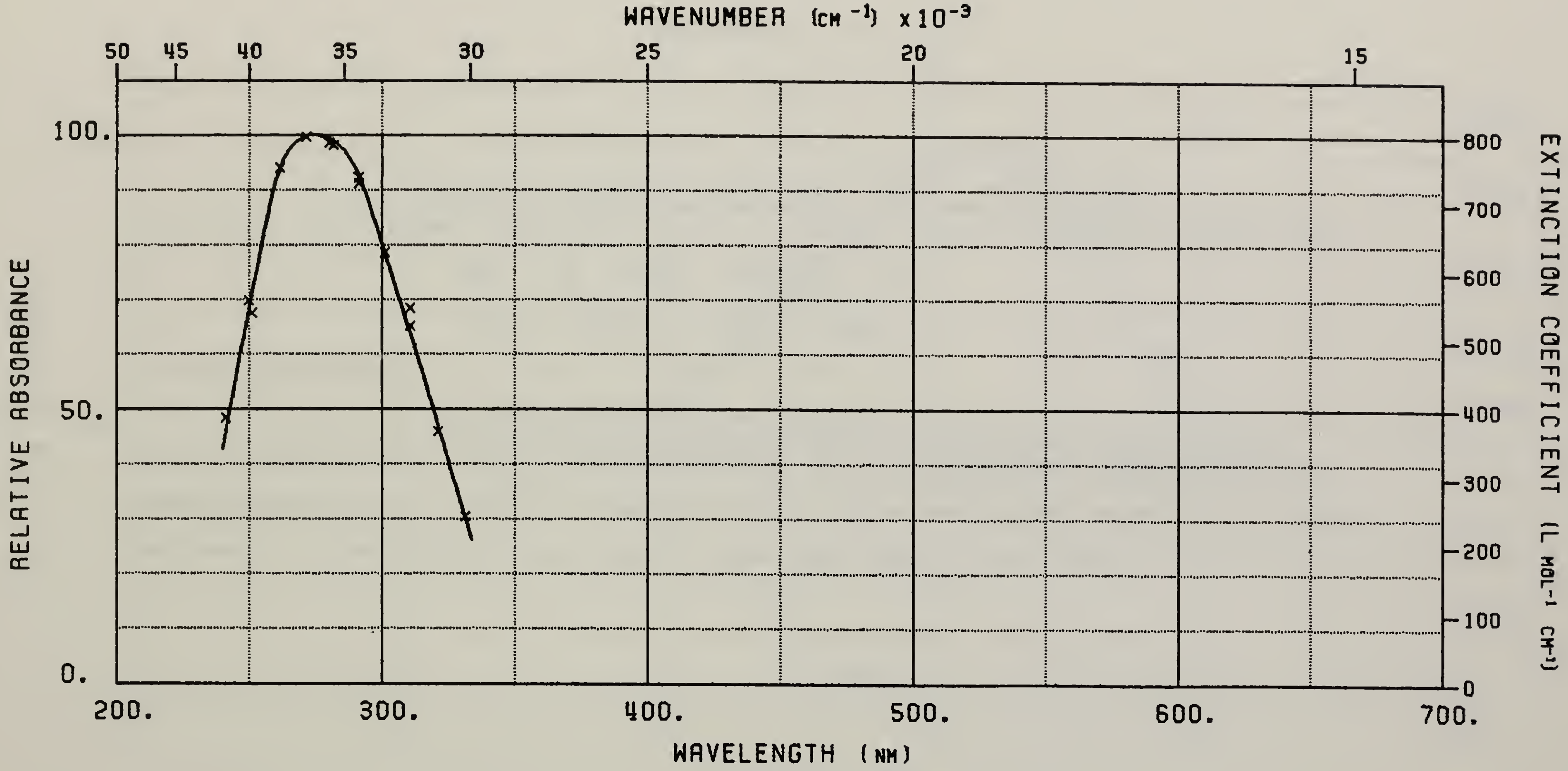
$$e(aq)^- + H_2P_2O_8{}^{2-} \rightarrow HPO_4{}^- + HPO_4{}^{2-}$$

$$HPO_4{}^- + H^+ \rightleftharpoons H_2PO_4,\ pK_a(H_2PO_4) = 5.7$$

Footnotes: [1] In other works where spectra were taken at shorter wavelengths, another peak was observed in the 300-400 nm region. For example see reference in footnote [2].

[2] G. Levey and E.J. Hart, J. Phys. Chem. 79(16): 1642-6 (1975).

$PO_5{}^{2-}$



Transient: $PO_5{}^{2-}$, peroxy phosphite radical anion, $\lambda(max)$ = 275 nm, ϵ_{275} = 800 L mol^{-1} cm^{-1}

System: aqueous solution of phosphite ions, containing oxygen, pH 9

PO_5^{2-}

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV; dose rate during pulse was 700 rad per μs.

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 QB PMT

Transient formation:

$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$

$OH + H_2PO_3^- \rightarrow HPO_3^- + H_2O$

$H + H_2PO_3^- \rightarrow HPO_3^- + H_2$

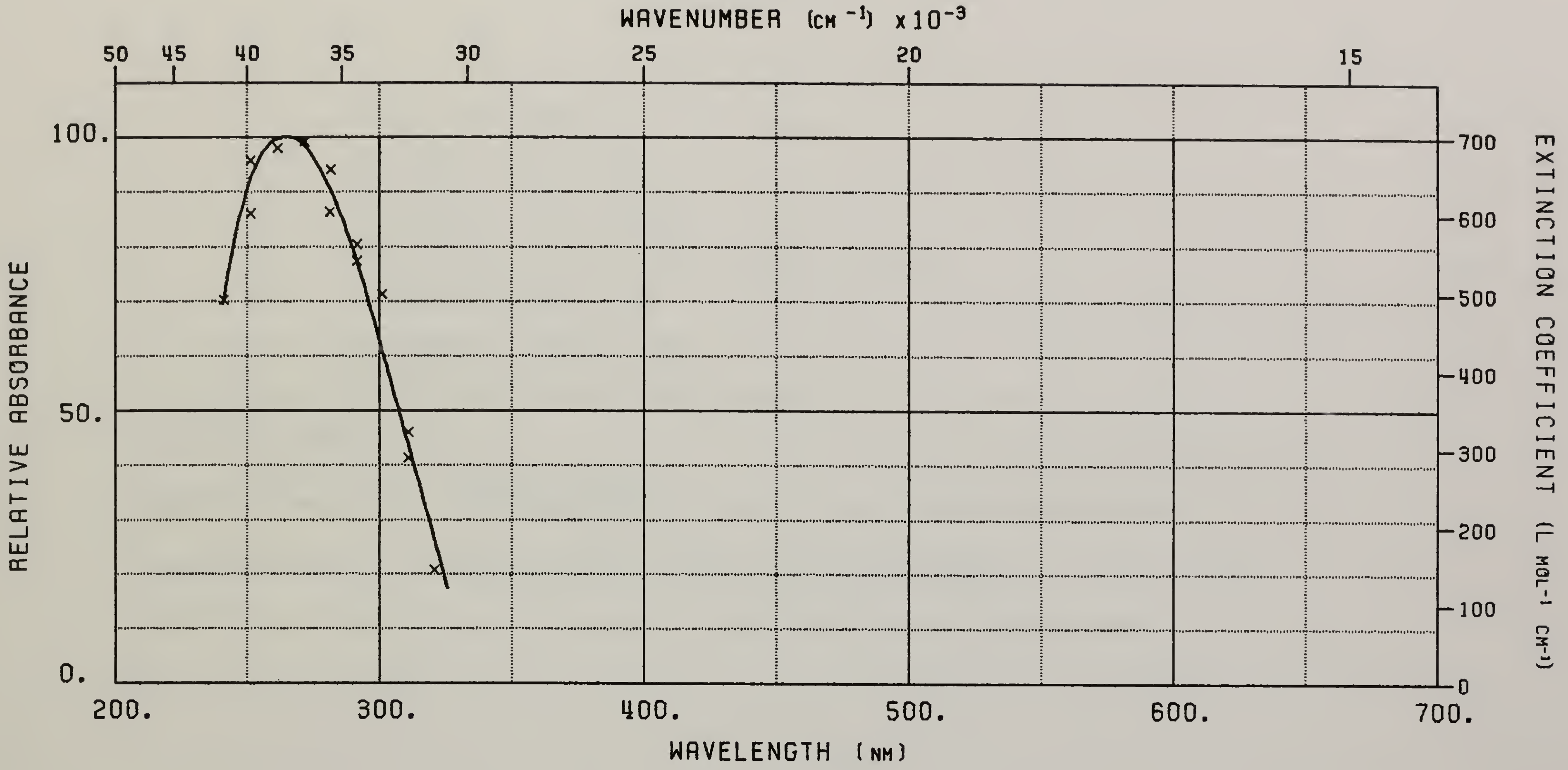
$OH^- + HPO_3^- \rightleftharpoons PO_3^{2-} + H_2O$, $pK_a(HPO_3^-) = 5.75$

$OH + HPO_3^{2-} \rightarrow H_2O + PO_3^{2-}$

$H + HPO_3^{2-} \rightarrow H_2 + PO_3^{2-}$

$PO_3^{2-} + O_2 \rightarrow PO_5^{2-}$

HPO_5^-



Transient: HPO_5^-, protonated peroxy phosphite radical anion, λ(max) = 265 nm,
ϵ_{265} = 700 L mol^{-1} cm^{-1}

System: aqueous solution of phosphite ions, containing oxygen, pH 2.5

HPO_5^-

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV; dose rate during pulse was 700 rad per μs

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 QB PMT

Transient formation:

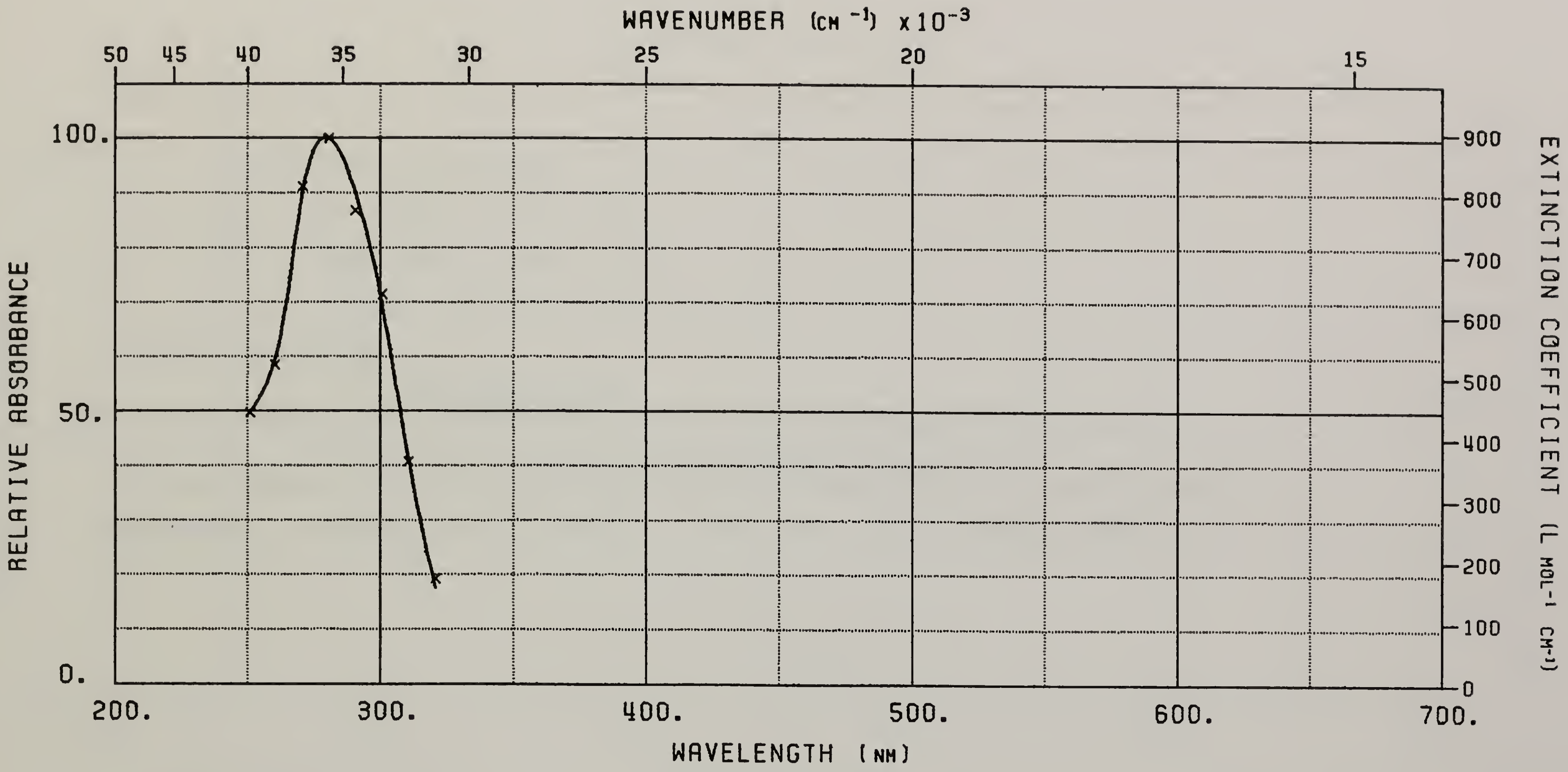
$$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + H_2PO_3^- \rightarrow HPO_3^- + H_2O$$

$$H + H_2PO_3^- \rightarrow HPO_3^- + H_2$$

$$HPO_3^- + O_2 \rightarrow HPO_5^-$$

ClO



Transient [1]: ClO, λ(max) ≈ 280 nm, ε_{280} ≈ 890 L mol^{-1} cm^{-1} [2,3]

System: aqueous solution of 10^{-3} mol L^{-1} ClO$^-$, Ar-saturated, pH 11.4

ClO

Reference: G.V. Buxton and M.S. Subhani, J. Chem. Soc., Faraday 1 68: 947-57 (1972)

Transient generation [4]: pulse radiolysis, Van de Graaff accelerator; dosimetry-secondary emission chamber [5]

Spectral acquisition [4]: monitoring lamp - Philips 150 W CSX xenon lamp; Bausch & Lomb f/3.5 high intensity, grating monochromator; EMI 9558 BQ PMT; Tektronix 545 oscilloscope with type B input preamplifier; bandwidth 10 nm

Transient formation:

$$e(aq)^- + ClO^- \rightarrow Cl^- + O^-$$

$$O^- + ClO^- + H_2O \rightarrow ClO + 2OH^-$$

$$e(aq)^- + ClO^- + H_2O \rightarrow Cl + 2OH^-$$

$$Cl + ClO^- \rightarrow ClO + Cl^-$$

$$H + ClO^- \rightarrow Cl^- + OH$$

$$OH + ClO^- \rightarrow ClO + OH^-$$

Footnotes:

[1] Spectrum was corrected for depletion of ClO^- which absorbs in the region of ClO absorption.

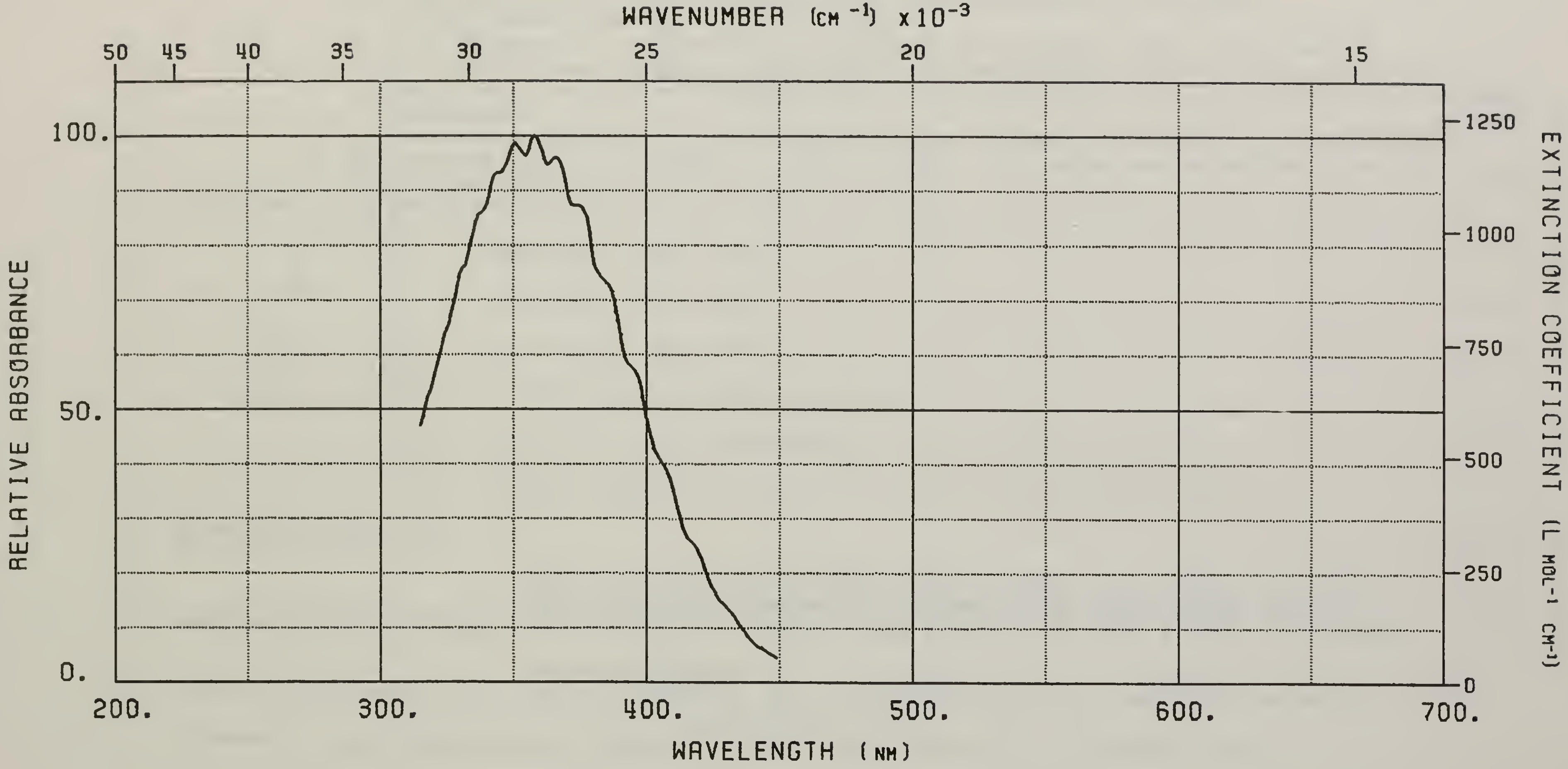
[2] Assuming $G(ClO) = G(e(aq)^-) + G(OH) + G(H)$. This value was calculated from the reaction mechanism by using measured product yields in a steady state radiolysis experiment.

[3] 890 L mol^{-1} cm^{-1} is the average of two extinction coefficients measured by the authors. The average was rounded to the nearest 10 L mol^{-1} cm^{-1}.

[4] K.W. Chambers, E. Collinson, F.S. Dainton, W.A. Seddon, and F. Wilkinson, Trans. Faraday Soc. 63: 1699-711 (1967).

[5] Calibrated by ferrocyanide dosimeter, using $G(Fe(CN)_6{}^{3-}) = 3.2$ and $\epsilon_{420}(Fe(CN)_6{}^{3-}) = 1000$ L mol^{-1} cm^{-1}.

ClO_2



Radical: ClO_2, $\lambda(max) \approx 360$, $\epsilon_{360} \approx 1000$ L mol^{-1} cm^{-1} [1]

System: aqueous solution of 1.5×10^{-3} mol L^{-1} ClO_2

ClO_2

Reference: F. Stitt, S. Friedlander, H.J. Lewis, and F.E. Young, Anal. Chem. 26(9): 1478-84 (1954)

Transient generation: radical is stable

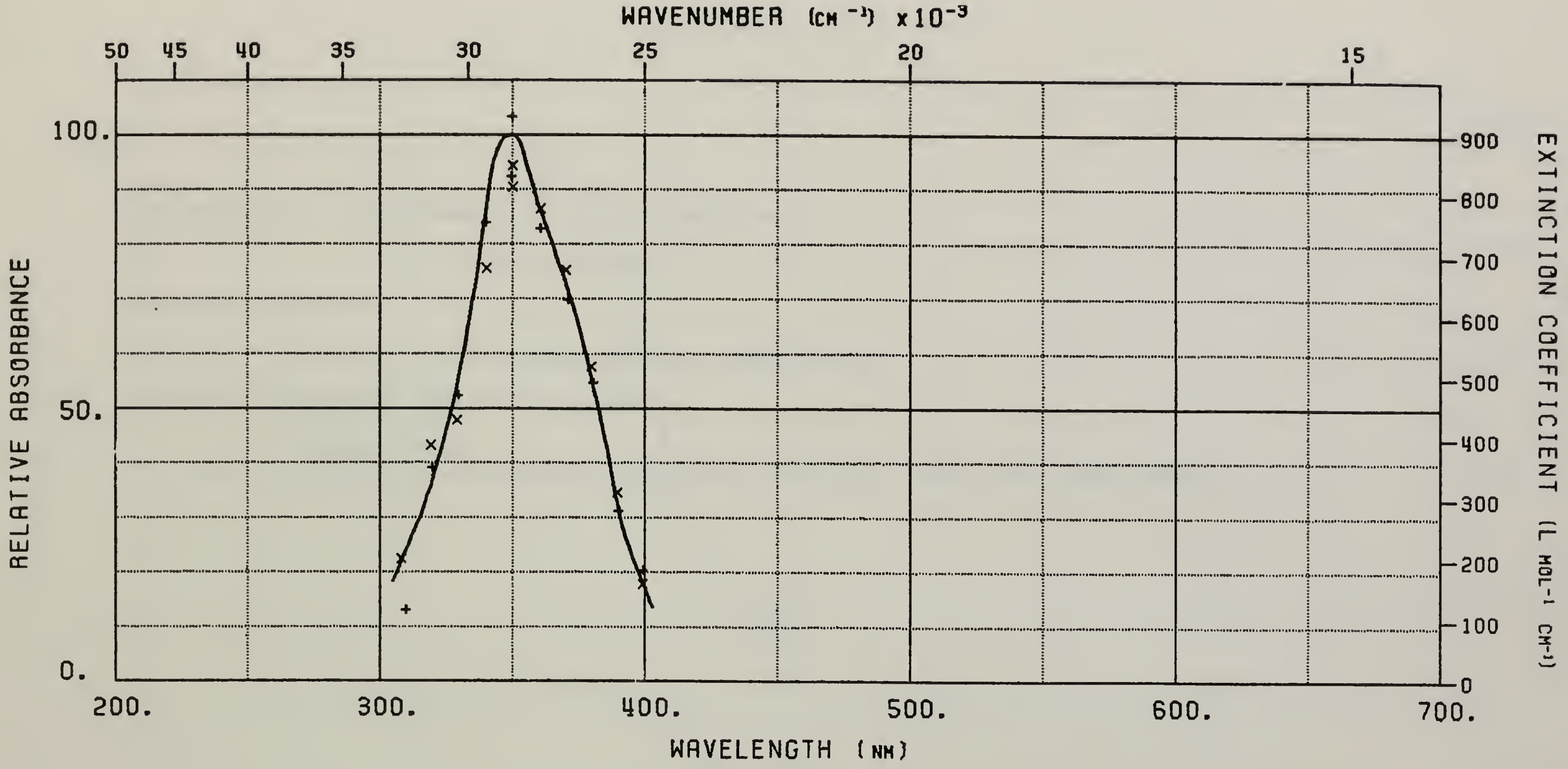
Spectral acquisition: Beckman Model DU spectrophotometer

Transient formation:

radical is stable

Footnote: [1] $\epsilon = 495\ L \cdot mol^{-1}\ cm^{-1}$ at $\lambda = 404.7$ nm.

BrO



Transient: BrO, λ(max) = 350 nm, ϵ_{350} ≈ 900 L mol^{-1} cm^{-1} [1]

System: aqueous 1.5 x 10^{-3} mol L^{-1} hypobromite [2]; data points represented by "x" are for 0.1 mol L^{-1} NaOH, and data points represented by "+" are for 10^{-3} mol L^{-1} NaOH

BrO

Reference: G.V. Buxton, F.S. Dainton, and F. Wilkinson, Chem. Commun. (11): 320-321 (1966)

Transient generation: pulse radiolysis; pulse energy 3 MeV

Spectral acquisition:

Transient formation [3]:

$$e(aq)^- + BrO^- \rightarrow Br^- + O^-$$

$$O^- + H_2O \rightleftharpoons OH + OH^-,\ pK_a(OH) = 11.85$$

$$OH + BrO^- \rightarrow OH^- + BrO$$

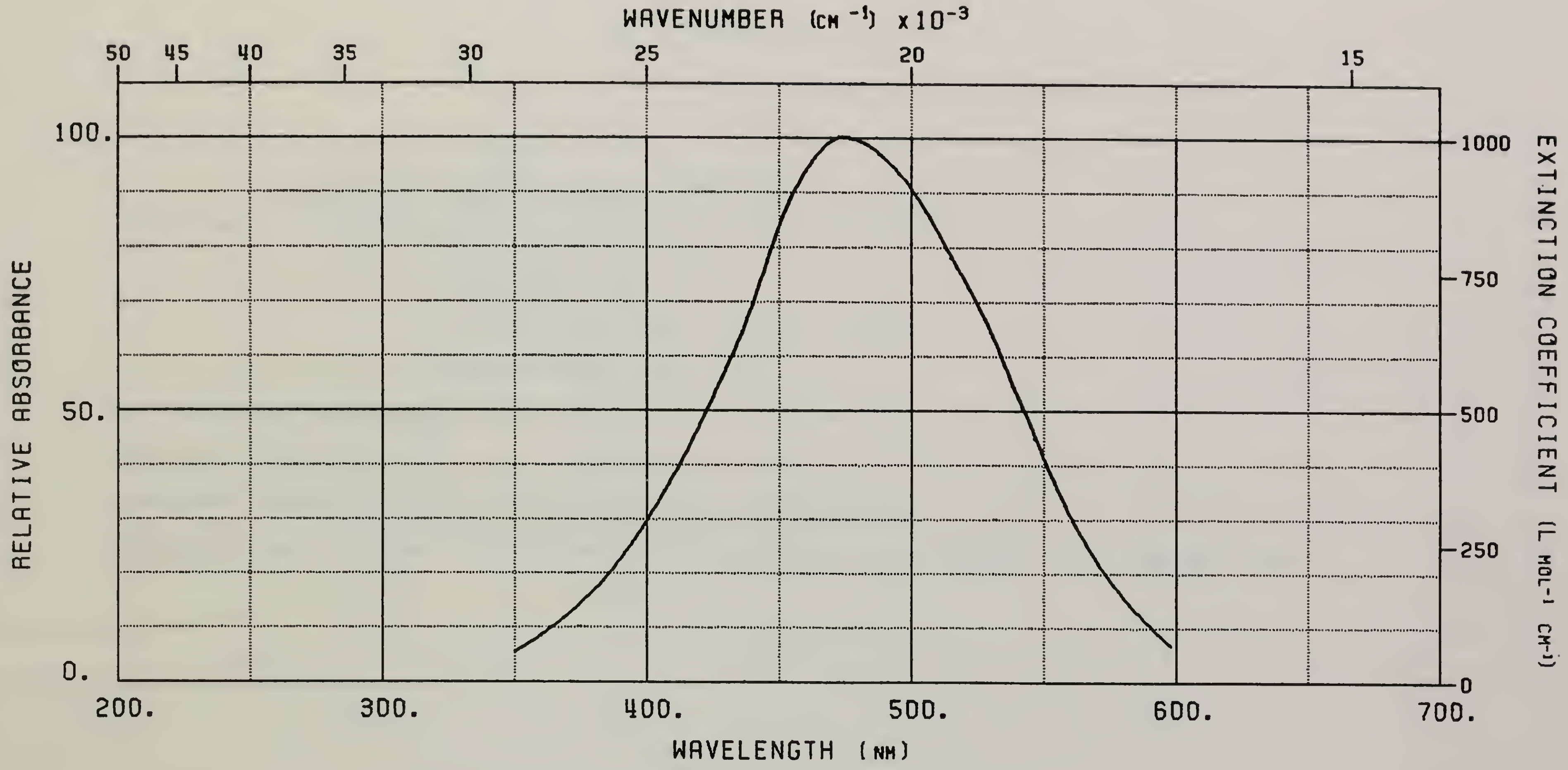
Footnotes:

[1] Using $G(e(aq)^-) + G(OH) \approx 6$.

[2] Br^- was removed from the solution by adding Ag^+.

[3] Written for 10^{-3} mol L^{-1} NaOH system.

BrO_2



Transient: BrO_2, λ(max) = 475 nm, ϵ_{475} = (1000 ± 100) L mol^{-1} cm^{-1} [1]

System: aqueous solution of BrO_3^-, saturated with Ar, pH neutral or alkaline

BrO_2

Reference: G.V. Buxton and F.S. Dainton, Proc. Roy. Soc. (London) Ser. A 304: 427-39 (1968)

Transient generation: pulse radiolysis, Van de Graaff accelerator; energy 2.9 MeV; syringe technique; dosimetry-secondary emission chamber [2]

Spectral acquisition [3]: monitoring lamp - Philips 150 W CSX xenon lamp; Bausch & Lomb f/3.5 high intensity, grating monochromator; EMI 9558 BQ PMT; Tektronix 545 oscilloscope with type B input preamplifier; bandwidth 10 nm

Transient formation:

$$e(aq)^- + BrO_3^- \ (+H_2O) \rightarrow (BrO_3^{2-} + H_2O) \rightarrow BrO_2 + 2OH^-$$

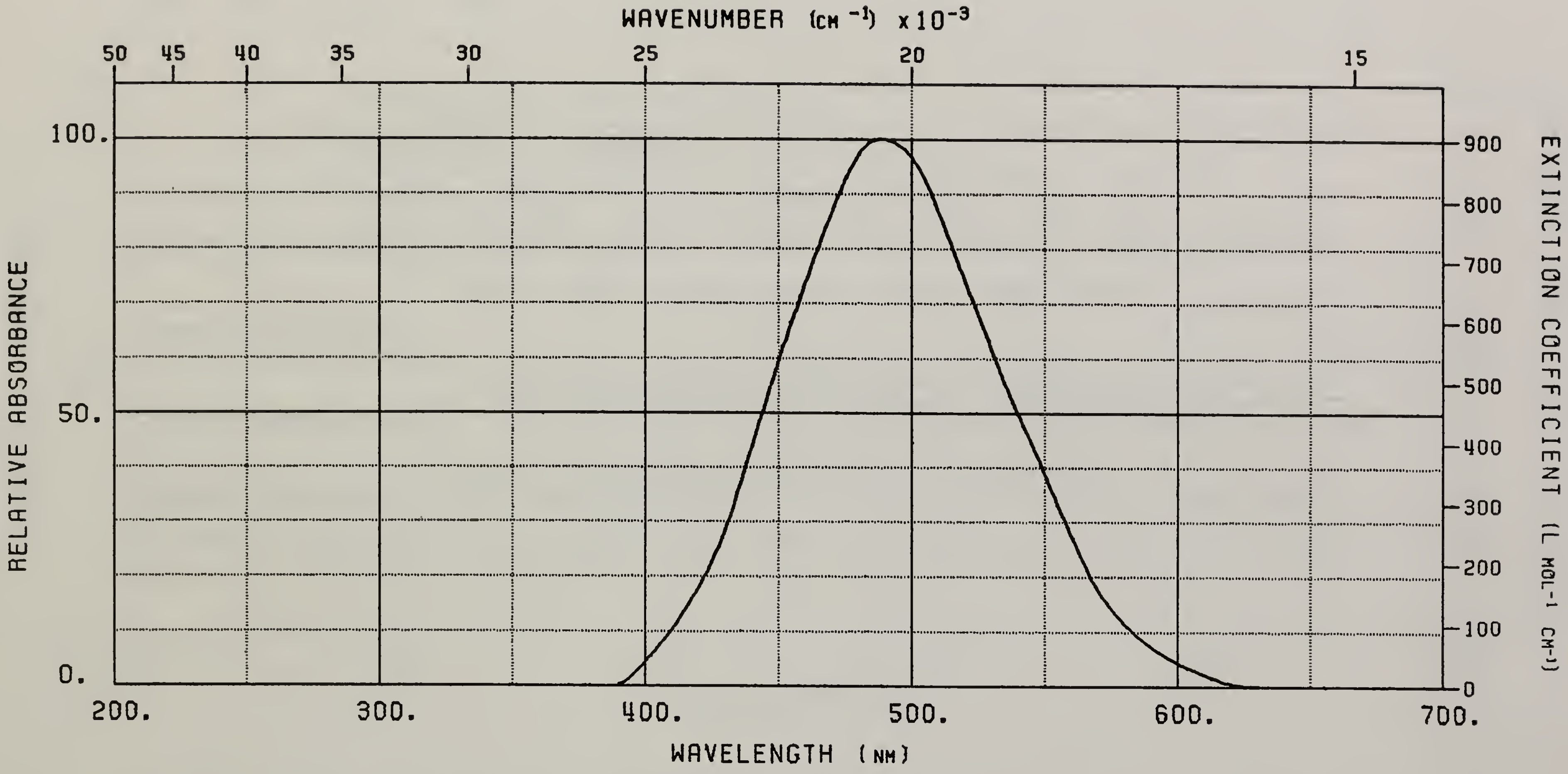
Footnotes:

[1] Based on assuming $G(BrO_2) = G(e(aq)^-) + G(H) + G(OH)$ for alkaline solutions of BrO_2^- and BrO_3^-. In these systems $OH + BrO_2^- \rightarrow BrO_2 + OH^-$ can occur in addition to the reduction of BrO_3^-.

[2] Calibrated by ferrocyanide dosimeter, using $G(Fe(CN)_6^{3-}) = 3.2$ and $\epsilon_{420}(Fe(CN)_6^{3-}) = 1000\ L\ mol^{-1}\ cm^{-1}$.

[3] K.W. Chambers, E. Collinson, F.S. Dainton, W.A. Seddon, and F. Wilkinson, Trans. Faraday Soc. 63: 1699-711 (1967).

IO



Transient: IO, λ(max) = 490 nm, ϵ_{490} = 900 ± 130 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 1.2 x 10^{-3} mol L^{-1} IO^{-}, pH = 13.6

IO

Reference: O. Amichai and A. Treinin, J. Phys. Chem. 74(4): 830-5 (1970)

Transient generation: pulse radiolysis (Varian linear accelerator); energy 5 MeV; pulse length 1.5 μs; dosimetry $K_4Fe(CN)_6$ [2]

Spectral acquisition: two Bausch & Lomb monochromators, type 567 AB; R136 and 1P28 PMT; split monitoring beam; spectrum was recorded at 5 nm intervals [3]; multiple reflections through cell, optical path 6 cm; time delay, 20 μs

Transient formation:

$IO^- + e(aq)^- \rightarrow I^- + O^-$

$OH^- + OH \rightarrow O^- + H_2O$, $pK_a(OH) = 11.85$

$O^- + IO^- \ (+H_2O) \rightarrow IO + 2OH^-$

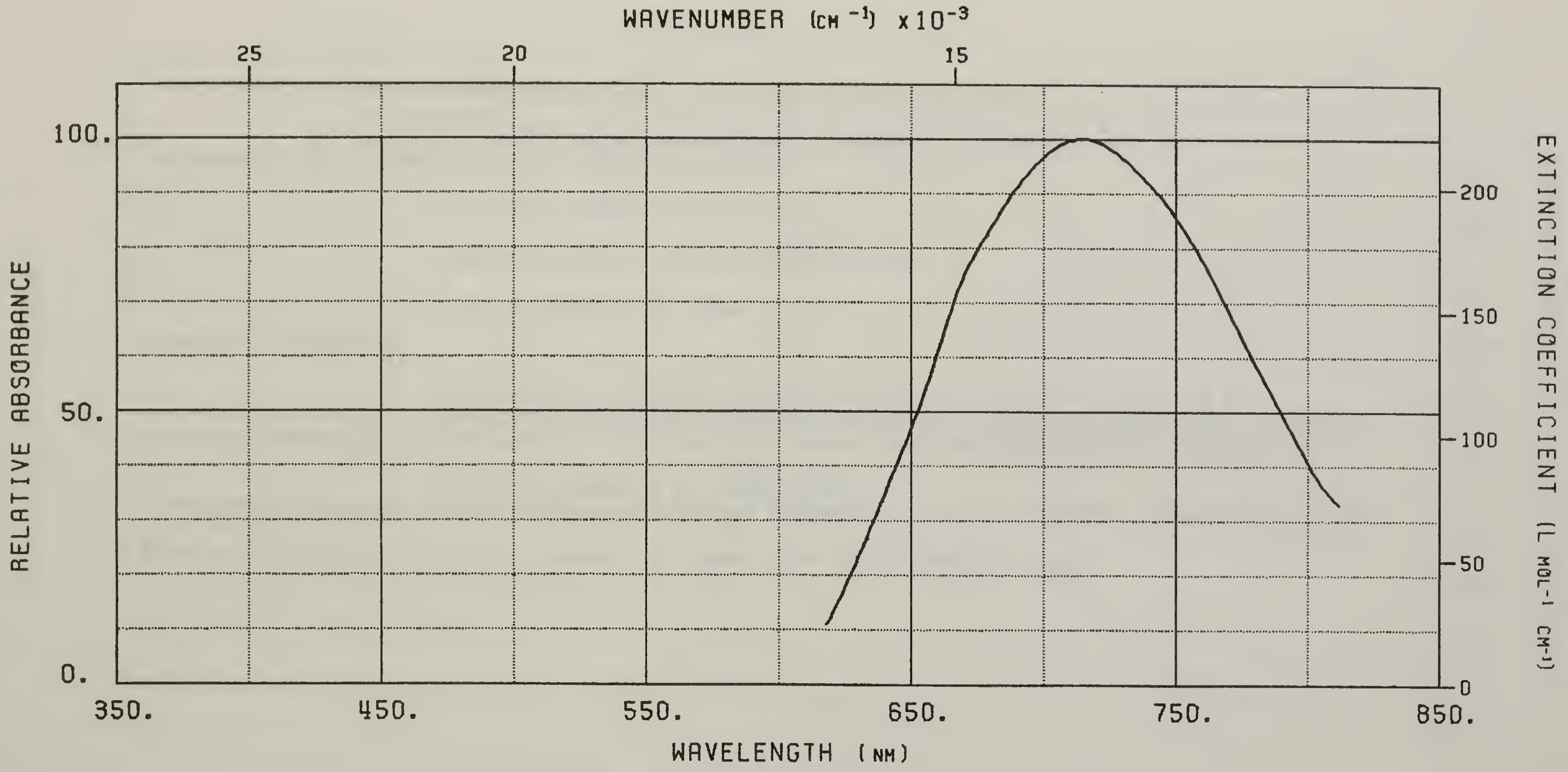
Footnotes:

[1] Assuming G(IO) = G(OH) + G(e(aq)$^-$)

[2] Dosimeter consisted of air-saturated $K_4Fe(CN)_6$ solution, taking $\epsilon_{420}(Fe(CN)_6{}^{3-}) = 1000$ L mol^{-1} cm^{-1} and $G(Fe(CN)_6{}^{3-}) = 2.7$.

[3] Experimental points were within 5% of smoothed curve.

IO_2



Transient [1]: IO_2[2], λ(max) = 715 nm, ϵ_{715} = (220 ± 30) L mol^{-1} cm^{-1} [3]

System: aqueous solution of 1.1 x 10^{-2} mol L^{-1} IO_3^-

IO_2

Reference: O. Amichai and A. Treinin, J. Phys. Chem. 74(4): 830-5 (1970)

Transient generation: pulse radiolysis (Varian linear accelerator); energy 5 MeV; pulse length 1.5 μs; dosimetry $K_4Fe(CN)_6$ [4]

Spectral acquisition: two Bausch 8 Lomb monochromators, type 567 AB; R136 and 1P28 PMT; split monitoring beam; spectrum was recorded at 5 nm intervals [5]; multiple reflections through cell, optical path 6 cm; time delay - 23 μs after pulse

Transient formation [6]:

$$e(aq)^- + IO_3^- \ (+H_2O) \rightarrow IO_2 + 2OH^-$$

Footnotes:

[1] In the flash photolysis of aqueous solutions of KIO_3, F. Barat, L. Gilles, B. Hickel, and J. Sutton, Chem. Commun. (24): 1485 (1969) assigned a spectrum having λ(max) = 480 nm to the IO_2 radical.

[2] The spectrum was a composite spectrum due to IO_3, IO, and IO_2. The IO_2 component was resolved by Gaussian fit on a wavenumber scale.

[3] From ratio of optical densities at zero time, $A(IO_2)/A(IO_3)$, the authors obtained $\epsilon(max)IO_2/\epsilon(max)IO_3 = 0.55 \pm 0.08$. For IO_3, $\epsilon(max) = (400 \pm 60)$ L mol^{-1} cm^{-1}, assuming $G(IO_3) = G(OH)$, see footnote 6.

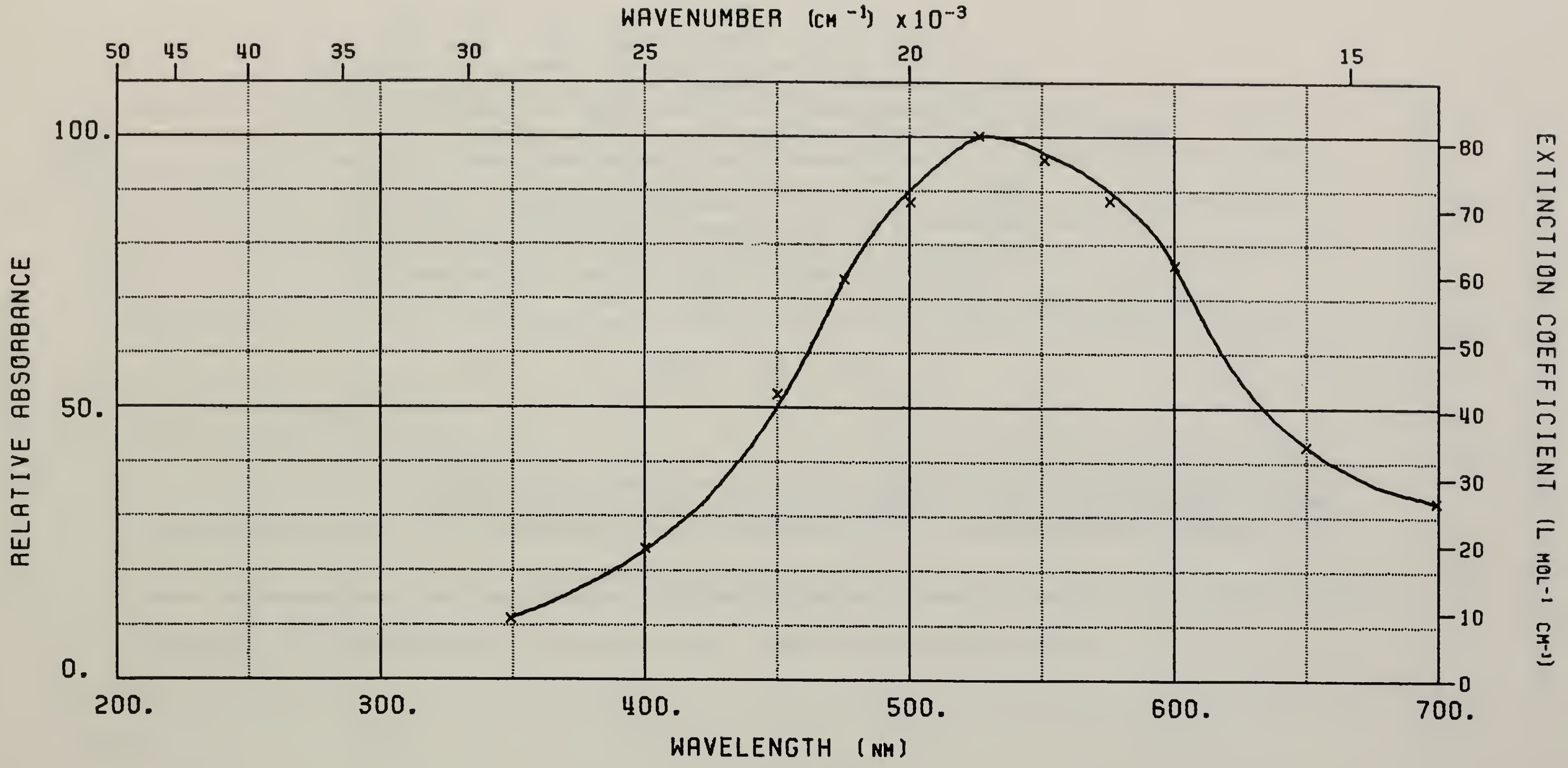
[4] Dosimeter consisted of air-saturated $K_4Fe(CN)_6$ solution, taking $\epsilon_{420}(Fe(CN)_6{}^{3-}) = 1000$ L mol^{-1} cm^{-1} and $G(Fe(CN)_6{}^{3-}) = 2.7$.

[5] Experimental points were within 5% of smoothed curve.

[6] Spectrum was complicated by absorption by IO_3 and IO

$$OH + IO_3^- \rightarrow IO_3 + OH^-$$
$$IO_2 + IO_3^- \rightarrow IO + IO_4^-$$

NH_2



Transient [1]: NH_2, amino radical, λ(max) = 530 nm, ϵ_{530} = 81 L mol^{-1} cm^{-1} [2]

System: aqueous solution of ammonia, N_2O saturated

NH_2

Reference: P.B. Pagsberg, RISO-256, Jan. 1972. p. 209-21 [Report, AEK-Riso, Roskilde, Denmark]

Transient generation: pulse radiolysis; dose rates during the pulse were 1-10 krad/μs; pulse length 0.4-2 μs; dosimetry-ferrocyanide [3]

Spectral acquisition: optical path length of 8 cm [4]

Transient formation:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + NH_3 \rightleftharpoons NH_2 + H_2O,\ pK_a(NH_3^+) = 2.3\ [5]$$

Footnotes:

[1] There was another band, that is not displayed, with a maximum at 215 nm. No extinction coefficient was given for this band, but it was assigned to the charge-transfer complexes (NH_2, H_2O) and (NH_2, NH_3).

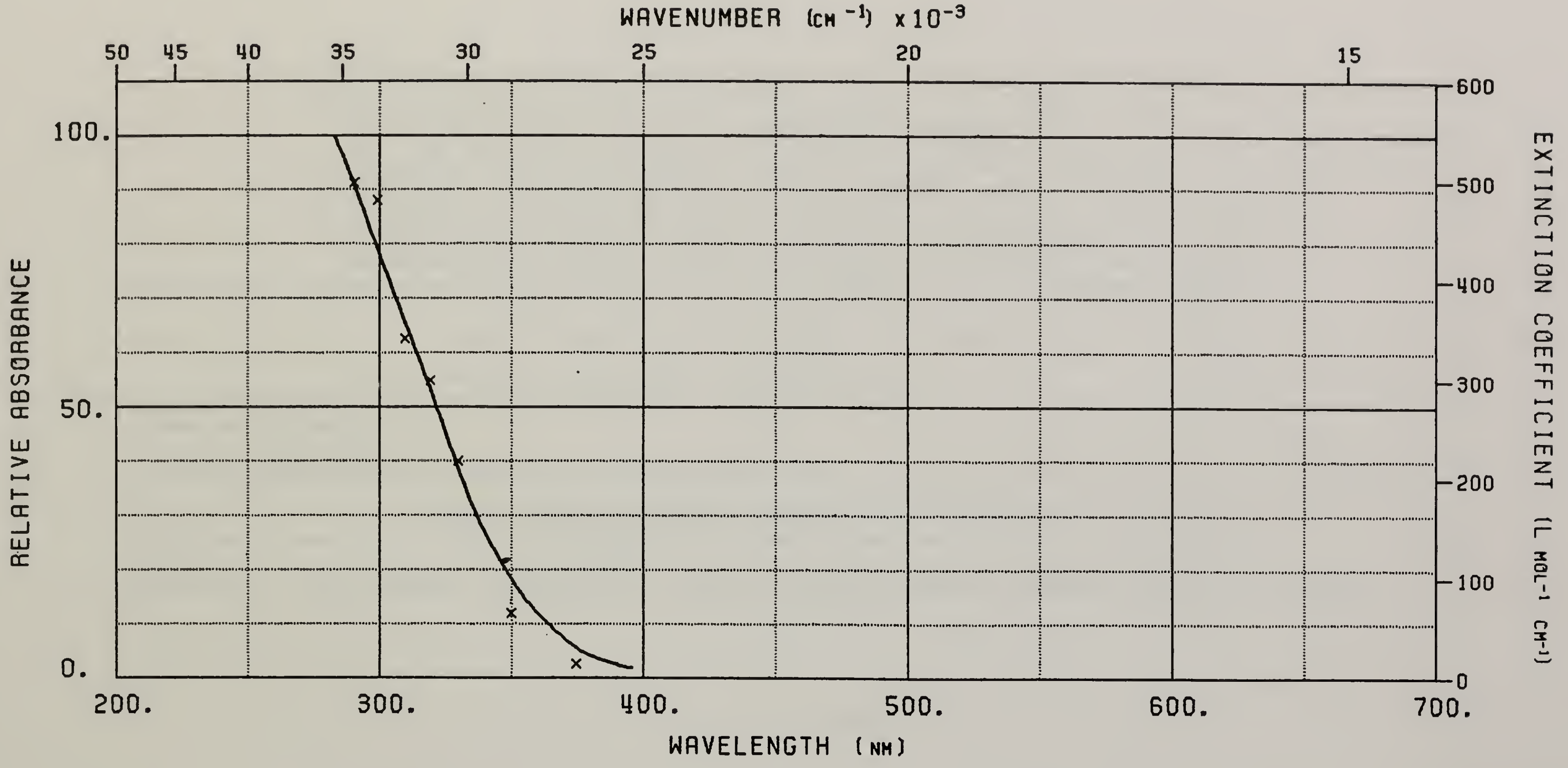
[2] Based on the solution to the rate equation for the above formation equations, assuming a constant production of OH during the pulse.

[3] Dosimeter consisted of aqueous solution of 10^{-3} mol L^{-1} $K_4Fe(CN)_6$, 2.5×10^{-2} mol L^{-1} N_2O, and about 10^{-4} mol L^{-1} O_2. $G(Fe(CN)_6{}^{3-})$ assumed to be equal to $G(e(aq)^-)$ + $G(OH)$ and ϵ_{420}(ferricyanide) = 1000 L mol^{-1} cm^{-1}.

[4] Optical densities were of the order of 0.03. The signal to noise ratio was 100.

[5] M.Z. Hoffman and K.R. Olson, J. Phys. Chem. 82(24): 2631-2 (1978).

NH_3^+



Transient: NH_3^+, protonated amino radical, $\epsilon_{290} \approx 500$ L mol^{-1} cm^{-1} [1], 2k ≈ 7 x 10^8 L mol^{-1} s^{-1}

System: aqueous solution of 2 x 10^{-5} mol L^{-1} $Co(NH_3)_6^{3+}$, pH 1 [2], deaerated

NH_3^+

Reference: M.Z. Hoffman and K.R. Olson, J. Phys. Chem. 82(24): 2631-2 (1978)

Transient generation: flash photolysis

Spectral acquisition: quartz-jacketed optical cell, path length 22 cm; time delay 50 μs after pulse

Transient formation [3]:

$$Co(III)(NH_3)_6^{3+} + h\nu \rightarrow Co(II)(NH_3)_5(NH_3^+)^{3+}$$

$$Co(II)(NH_3)_5(NH_3^+)^{3+}\ (+5H^+) \rightarrow Co(aq)^{2+} + 5NH_4^+ + NH_3^+$$

$$NH_3^+ \rightleftharpoons NH_2 + H^+,\ pK_a(NH_3^+) = 2.3\ [4]$$

Footnotes:

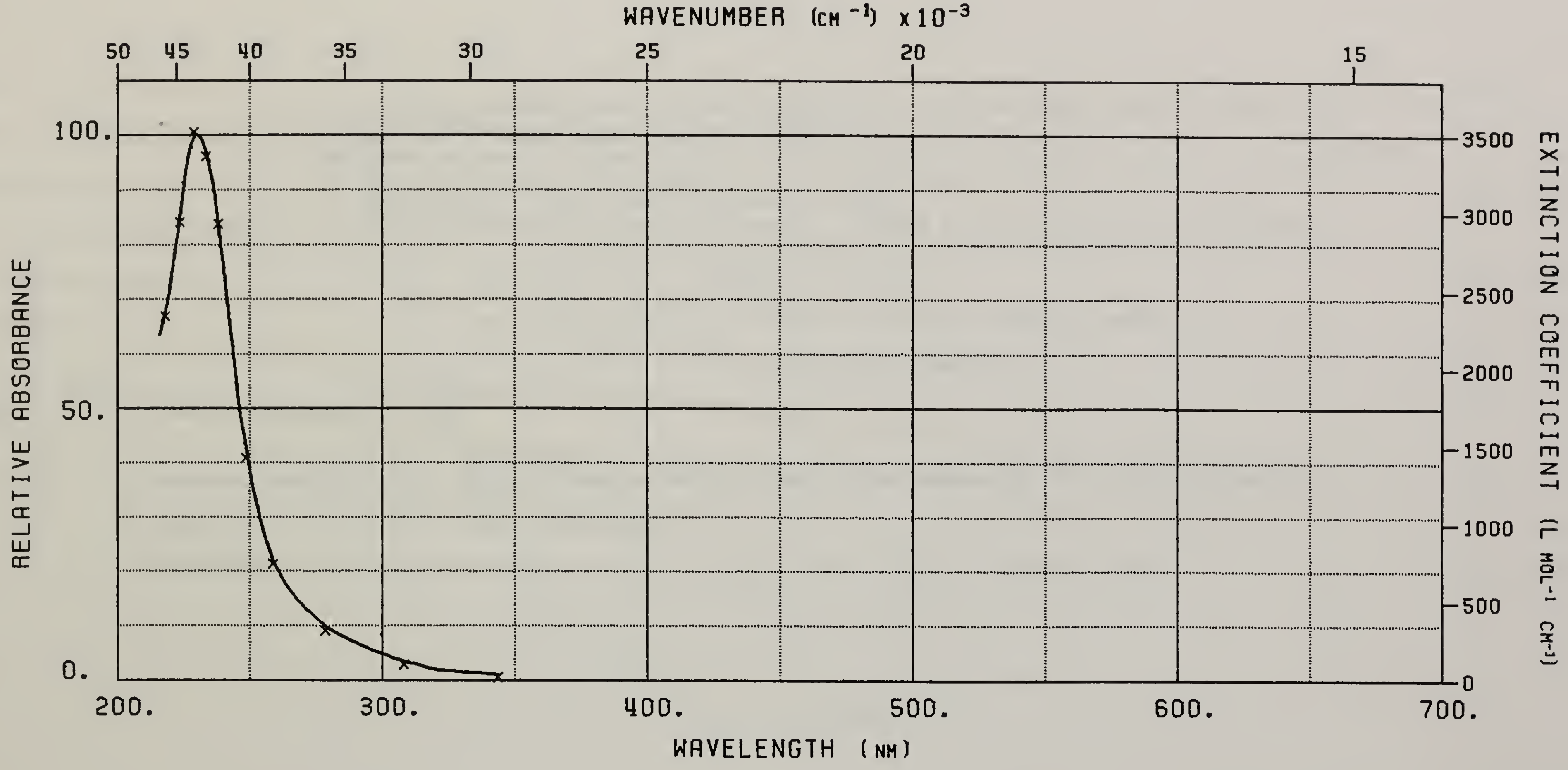
[1] Based on ≈ 4 x 10^{-6} mol L^{-1} $Co(aq)^{2+}$ formed as determined by the method of R.E. Kitson, Anal. Chem. 22: 664-7 (1950)

[2] Acidity adjusted with $HClO_4$.

[3] Quantum yield at 254 nm = 0.16, M.F. Manfrin, G. Varani, L. Moggi, and V. Balzani, Mol. Photochem. 1(4): 387-402 (1969).

[4] At pH 4, absorption spectrum could not be distinguished from scattered light.

N_2H_3



Transient: N_2H_3, hydrazyl radical, λ(max) = 230 nm, ϵ_{230} = 3500 L mol^{-1} cm^{-1} [1],
$2k = 2.4 \times 10^9$ L mol^{-1} s^{-1}

System: aqueous solution of 2×10^{-2} mol L^{-1} N_2H_4, N_2O (1 atm), pH 9.2

N_2H_3

Reference: E. Hayon and M. Simic, J. Am. Chem. Soc. 94(1): 42-7 (1972)

Transient generation: pulse radiolysis, Febetron 705; pulse energy 2.3 MeV; pulse length ≈ 30 ns; dose ≈ 8 krad per pulse; dosimetry KSCN

Spectral acquisition: double monochromator; 450 W xenon lamp, pulsed to increase output by a factor of ≈ 20-25; time delay ≈ 0.1 μs after pulse

Transient formation:

$N_2O + e(aq)^- \; (+H_2O) \rightarrow N_2 + OH^- + OH$

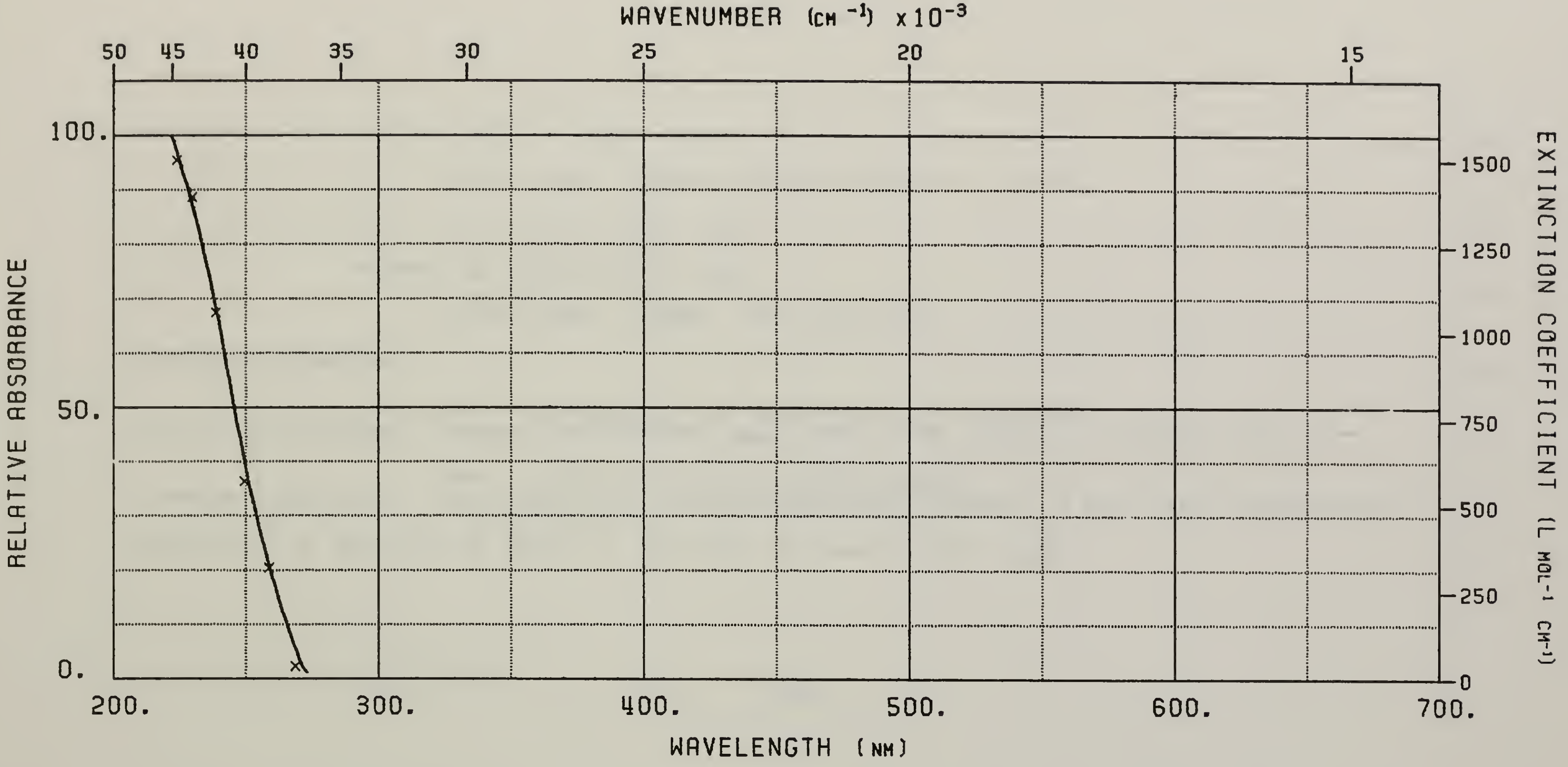
either $OH + N_2H_4 \rightarrow N_2H_3 + H_2O$

or $OH + N_2H_4 \rightarrow N_2H_4^+ + OH^-$

$N_2H_4^+ + OH^- \rightleftharpoons N_2H_3 + H_2O$, $pK_a(N_2H_4^+) = 7.1 \pm 0.1$

Footnote: [1] Using $G(e(aq)^-) = G(OH) = 2.8$.

$N_2H_4^+$



Transient: $N_2H_4^+$, ϵ_{225} = 1500 L mol^{-1} cm^{-1} [1], 2k = 6.0 x 10^{8} L mol^{-1} s^{-1}

System: aqueous solution of 2 x 10^{-2} mol L^{-1} N_2H_4, N_2O (1 atm), pH 3.7

$N_2H_4^+$

Reference: E. Hayon and M. Simic, J. Am. Chem. Soc. 94(1): 42-7 (1972)

Transient generation: pulse radiolysis, Febetron 705; pulse energy 2.3 MeV; pulse length ≈ 30 ns; dose ≈ 8 krad per pulse; dosimetry KSCN

Spectral acquisition: double monochromator; 450 W xenon lamp, pulsed to increase output by a factor of ≈ 20-25; time delay ≈ 0.1 μs after pulse

Transient formation:

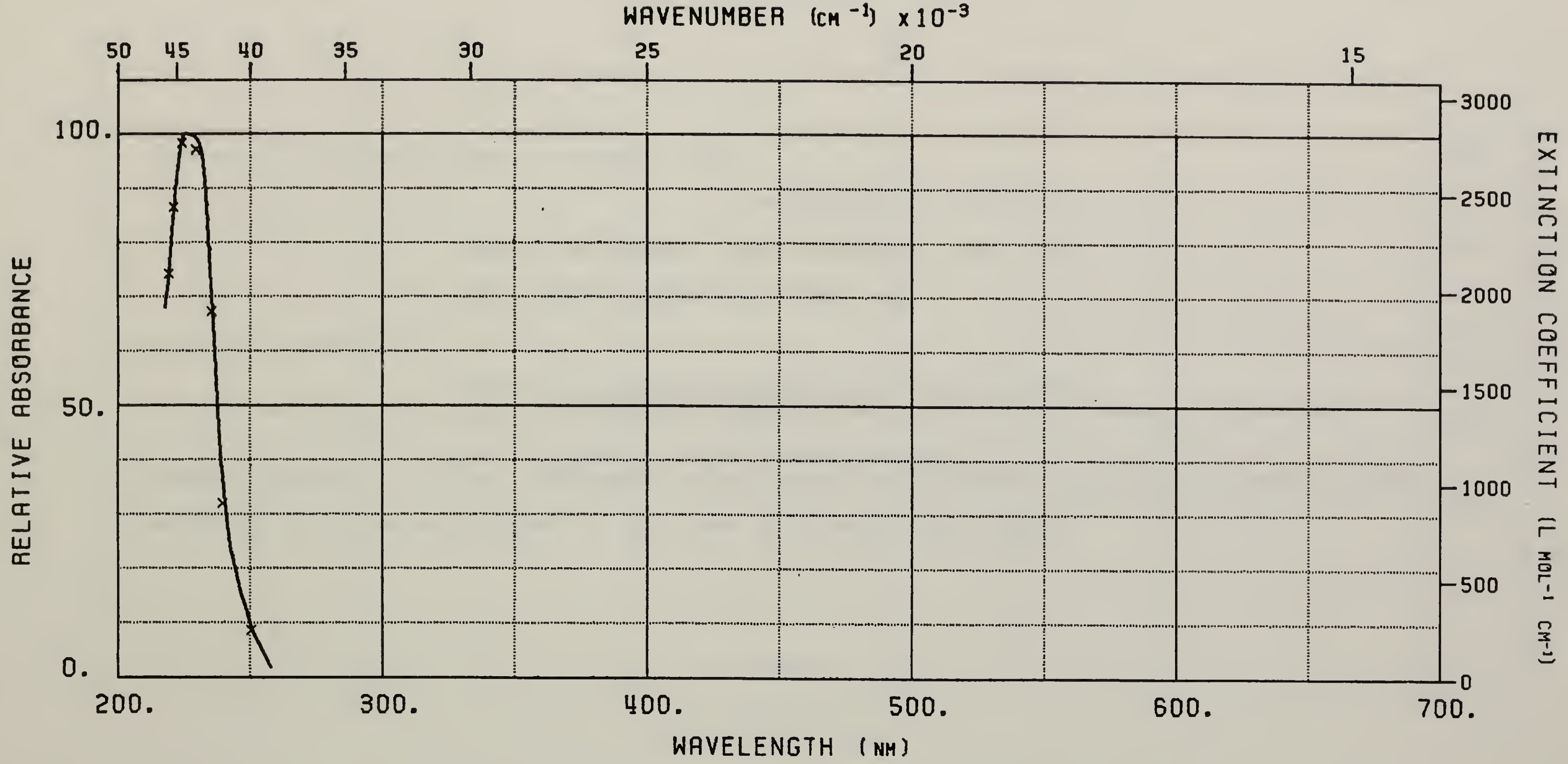
$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$N_2H_5^+ + OH \rightarrow N_2H_4^+ + H_2O, \ pK_a(N_2H_5^+) = 8.1 \pm 0.1$$

$$\text{and } pK_a(N_2H_4^+) = 7.1 \pm 0.1$$

Footnote: [1] Using $G(e(aq)^-) = G(OH) = 2.8$.

N_3H_3



Transient: N_3H_3, $\lambda(\text{max})$ = 225 nm, ϵ_{225} = 2800 L mol^{-1} cm^{-1}

System: aqueous solution of 2 x 10^{-2} mol L^{-1} N_2H_4, N_2O (1 atm), pH 9.2

N_3H_3

Reference: E. Hayon and M. Simic, J. Am. Chem. Soc. 94(1): 42-7 (1972)

Transient generation: pulse radiolysis, Febetron 705; pulse energy 2.3 MeV; pulse length ≈ 30 ns; dose ≈ 8 krad per pulse; dosimetry KSCN

Spectral acquisition: double monochromator; 450 W xenon lamp, pulsed to increase output by a factor of ≈ 20-25; time delay 10 ms after pulse

Transient formation:

$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$

$OH + N_2H_4 \rightarrow N_2H_3 + H_2O$ [1]

$2N_2H_3 \rightleftharpoons N_4H_6$ [2]

$N_4H_6 + H_2O \rightleftharpoons N_4H_7^+ + OH^-$

$N_4H_7^+ + H_2O \rightleftharpoons N_4H_8^{2+} + OH^-$

$N_4H_8^{2+} + H_2O \rightarrow NH_3 + N_3H_4^+ + H_3O^+$

$OH^- + N_3H_4^+ \rightleftharpoons N_3H_3 + H_2O$, $pK_a(N_3H_4^+) = 7.0 \pm 0.2$

Footnotes: [1] Alternative formation of N_2H_3 radical is

$OH + N_2H_4 \rightarrow N_2H_4^+ + OH^-$

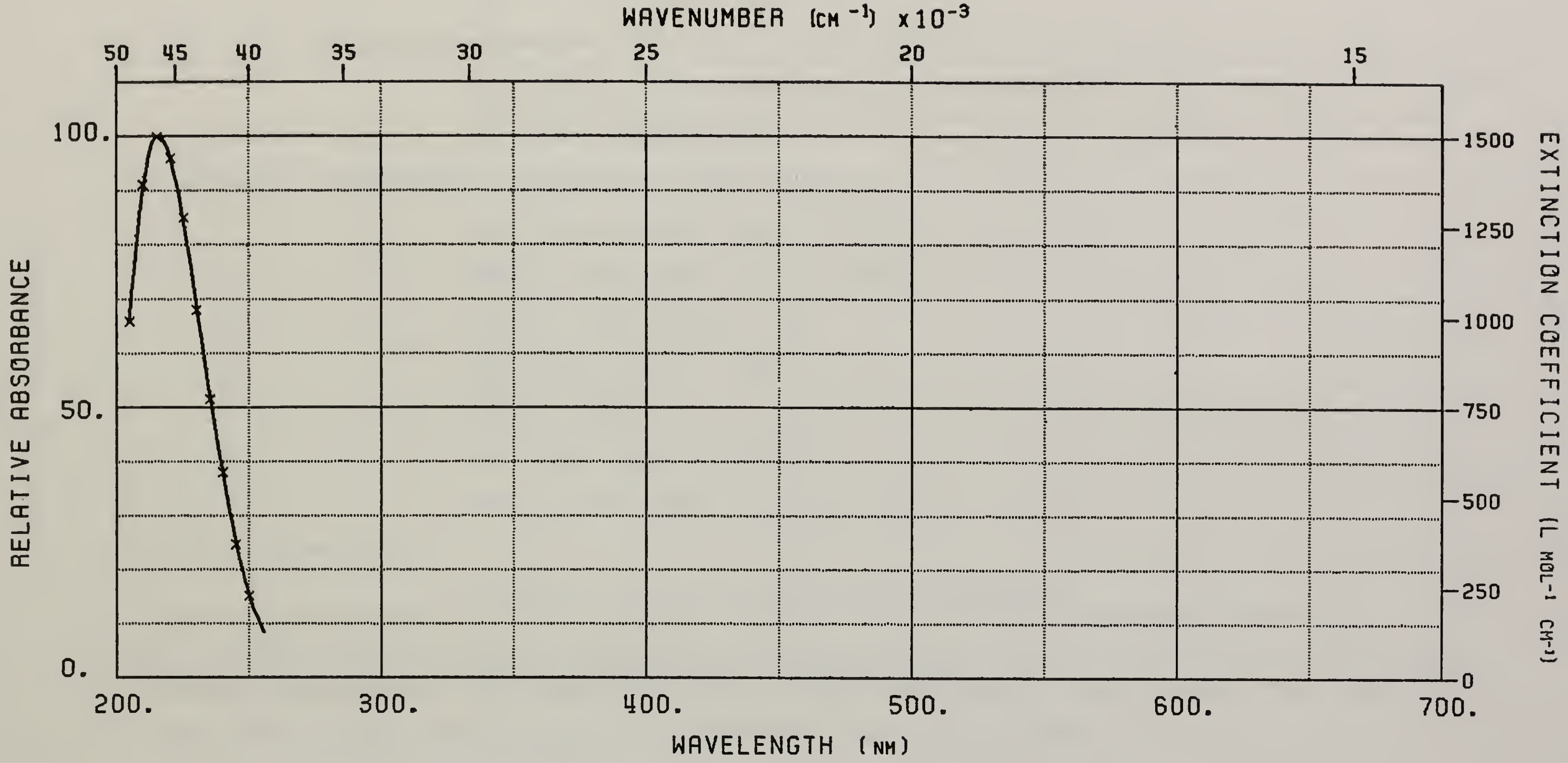
$OH^- + N_2H_4^+ \rightleftharpoons N_2H_3 + H_2O$, $pK_a(N_2H_4^+) = 7.1 \pm 0.1$.

[2] Disproportionation

$2N_2H_3 \rightarrow N_2H_2 + N_2H_4$

was ruled out because N_2H_2 should give an equivalent amount of N_2 and H_2, and this was not observed.

NHOH or H_2NO



Transient [1]: NHOH[2] or H_2NO[3], λ(max) = 216 nm, $\epsilon_{216} \approx 1500$ L mol^{-1} cm^{-1} [4,5]

System: aqueous solution of 10^{-3} mol L^{-1} hydroxylamine, 2 x 10^{-2} mol L^{-1} N_2O, pH 7.6 or 5.4 [6]

$NHOH$ or H_2NO

Reference: D.Behar, D. Shapira, and A. Treinin, J. Phys. Chem. 76(2): 180-6 (1972)

Transient generation: pulse radiolysis, using linear accelerator; pulse energy 5 MeV; dosimetry modified Fricke [8]

Spectral acquisition: 60 W deuterium monitoring lamp; "solar blind" R166 PMT [9]

Transient formation [10]:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + NH_2OH \rightarrow NHOH\ (\text{or } H_2NO) + H_2O\ [11]$$

Footnotes:

[1] Due to conflicts between information given in footnotes 2 and 3, the assignment of the spectrum is currently in doubt. P. Neta, private communication, 1978.

[2] Simic and Hayon [7] assigned the spectrum to NHOH and not to H_2NO because (a) the similarity of the spectra of the intermediates formed in the reaction of OH with NH_2OH and NH_2OCH_3 and (b) the large difference in the acid-base properties of these two radicals from NH_2OH and NH_2OCH_3. Simic and Hayon used (a) and (b) to suggest that the radicals from NH_2OH and NH_2OCH_3 are NHOH and $NHOCH_3$, respectively.

[3] From esr data O.P. Chawla and R.W. Fessenden, J. Phys. Chem. 79(24): 2693-700 (1975) assigned the radical, observed from the reaction of NH_2OH with SO_4^-, as H_2NO.

[4] Measurement at 230 nm gave ϵ_{230} = (1020 ± 30) L mol^{-1} cm^{-1} at pH 5.5.

[5] Another value was reported in the literature, ϵ_{217} = 2500 L mol^{-1} cm^{-1} [7].

[6] Each data point is the average of six measurements, three measurements at each pH. The scatter of these points was ±5%.

[7] M. Simic and E. Hayon, J. Am. Chem. Soc. 93: 5982-6 (1971).

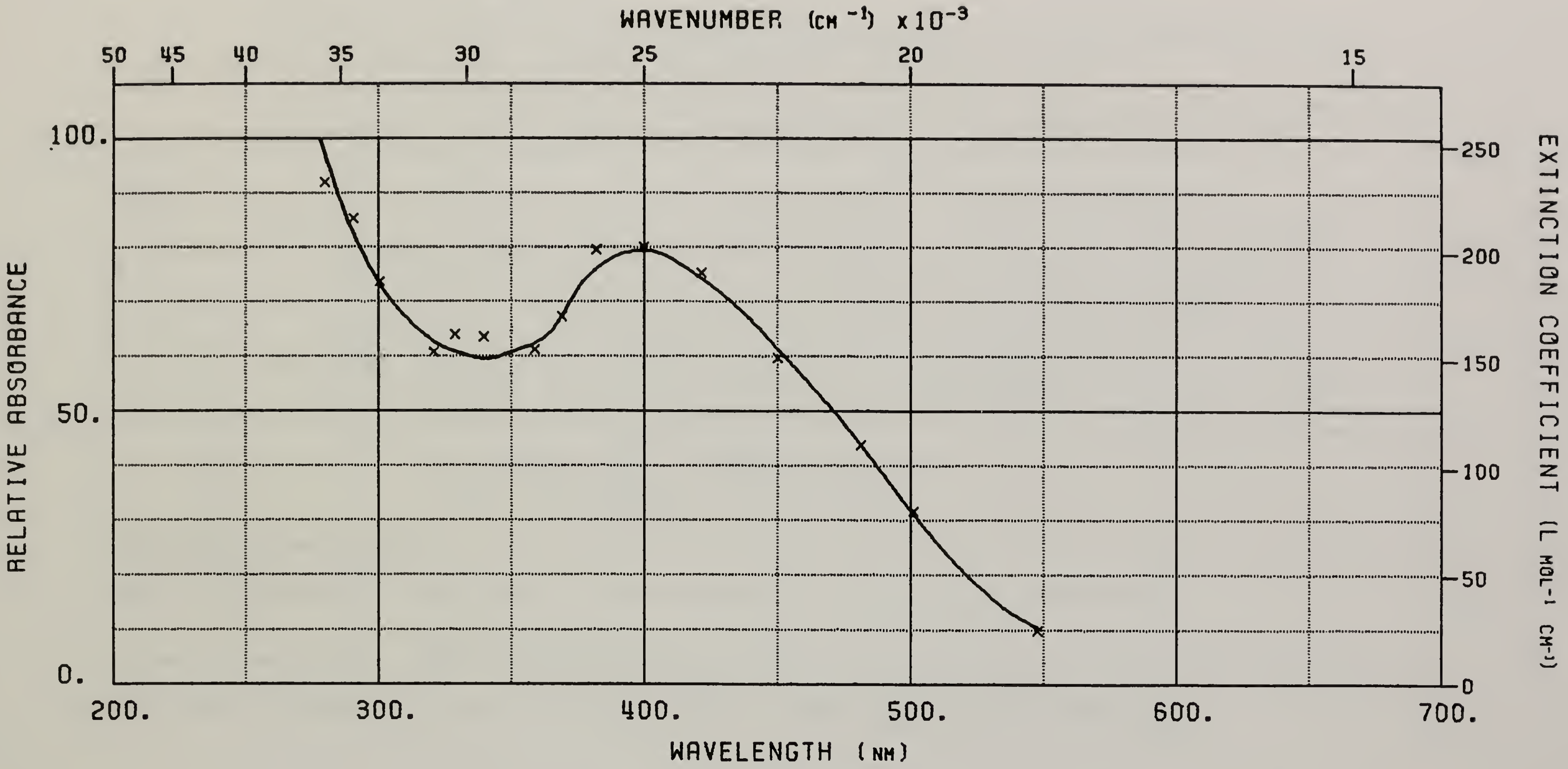
[8] M.S. Matheson and L.M. Dorfman, Pulse Radiolysis, MIT Press, Cambridge, 1969.

[9] Corrections were made for stray light.

[10] Written for pH 7.6.

[11] $pK_a(NH_3OH^+) = 6.0 \pm 0.1$ and $pK_a(NH_2OH^+) = 4.2 \pm 0.1$.

NO_2



Transient: NO_2, $\lambda(\mathrm{max}) = 400$ nm, $\epsilon_{400} = 201$ L mol^{-1} cm^{-1}, $2k = (9.0 \pm 2.0) \times 10^8$ L mol^{-1} s^{-1}

System: aqueous solution of NO_2^-, saturated with N_2O

NO_2

Reference: M. Graetzel, A. Henglein, J. Lilie, and G. Beck, Ber. Bunsenges. Physik. Chem. 73(7): 646-53 (1969)

Transient generation: pulse radiolysis [1] using Van de Graaff generator; energy 1.6 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

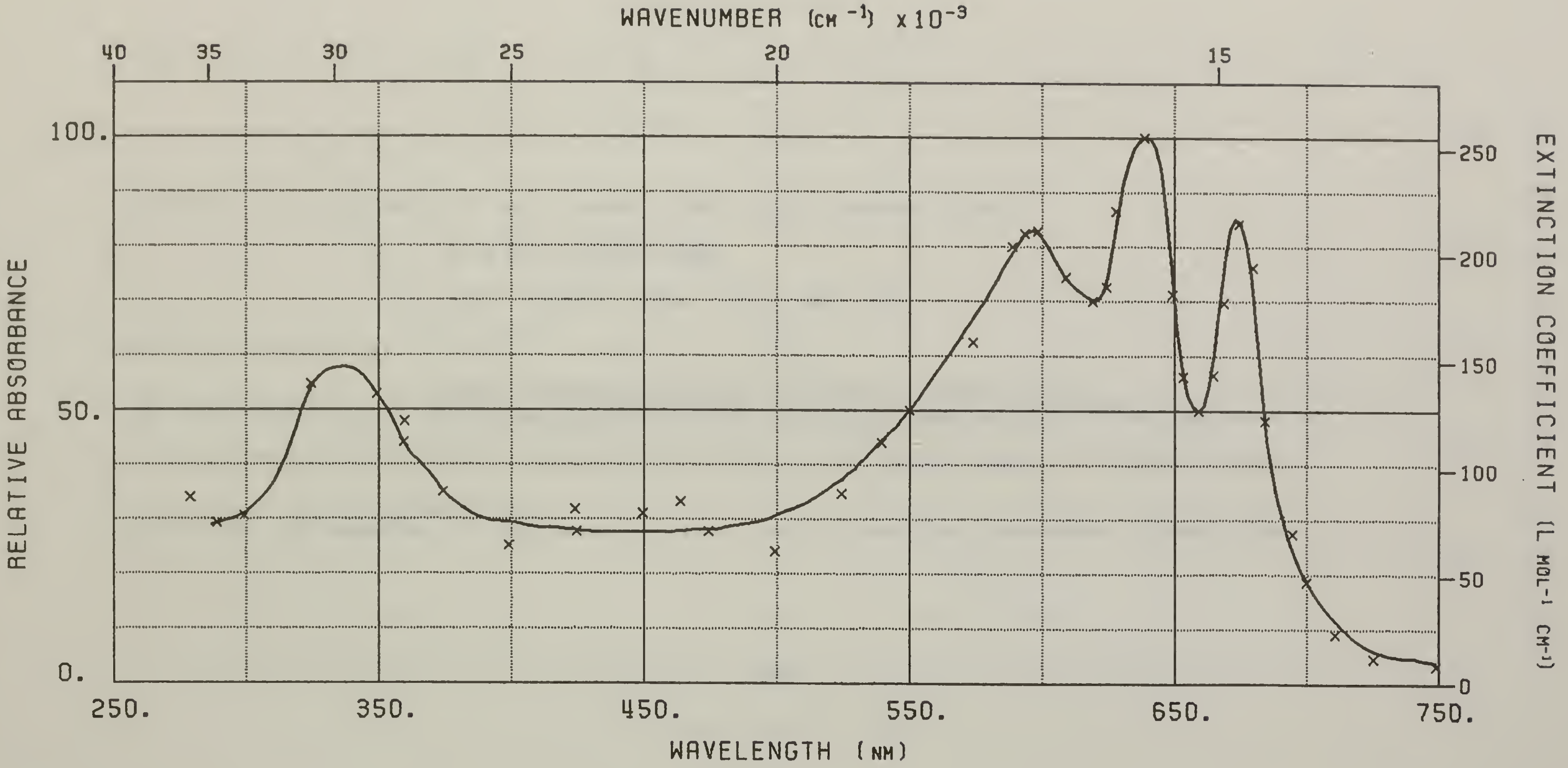
Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + NO_2^- \rightarrow OH^- + NO_2$$

Footnote: [1] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

NO_3



Transient [1]: NO_3, λ(max) = 595, 640, 675 nm, ϵ_{635} = (250 ± 90) L mol^{-1} cm^{-1} [2]

System: aqueous solution of 0.1 mol L^{-1} $K_2Ce(NO_3)_6$, pH 0.65 [3]

NO_3

Reference: L. Dogliotti and E. Hayon, J. Phys. Chem. 71: 3802-8 (1967)

Transient generation [4]: flash photolysis; oxygen flash lamp with total energy 1800 J per flash; total flash duration 70 μs, duration at "1/e time" 5 μs

Spectral acquisition [4]: Bausch 8 Lomb 250 nm grating monochromator; Osram 450 W xenon monitoring lamp, attention given to minimize exposure of the solution to this lamp; EMI 9552 B PMT; Tektronix 535A oscilloscope, traces recorded on film; time delay 200 μs after start of flash

Transient formation [5,6]:

$$Ce(IV)\cdot NO_3^- + h\nu \rightarrow [Ce(III)\cdots NO_3]^*$$

$$[Ce(III)\cdots NO_3]^* \rightarrow Ce(III) + NO_3$$

Footnotes:

[1] Band at 340 nm was tentatively suggested to be due to N_2O_4, not NO_3. R.K. Broszkiewicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim. 24(3): 221-9 (1976).

[2] R.W. Glass and T.W. Martin, J. Am. Chem. Soc. 92: 5084-93 (1970).

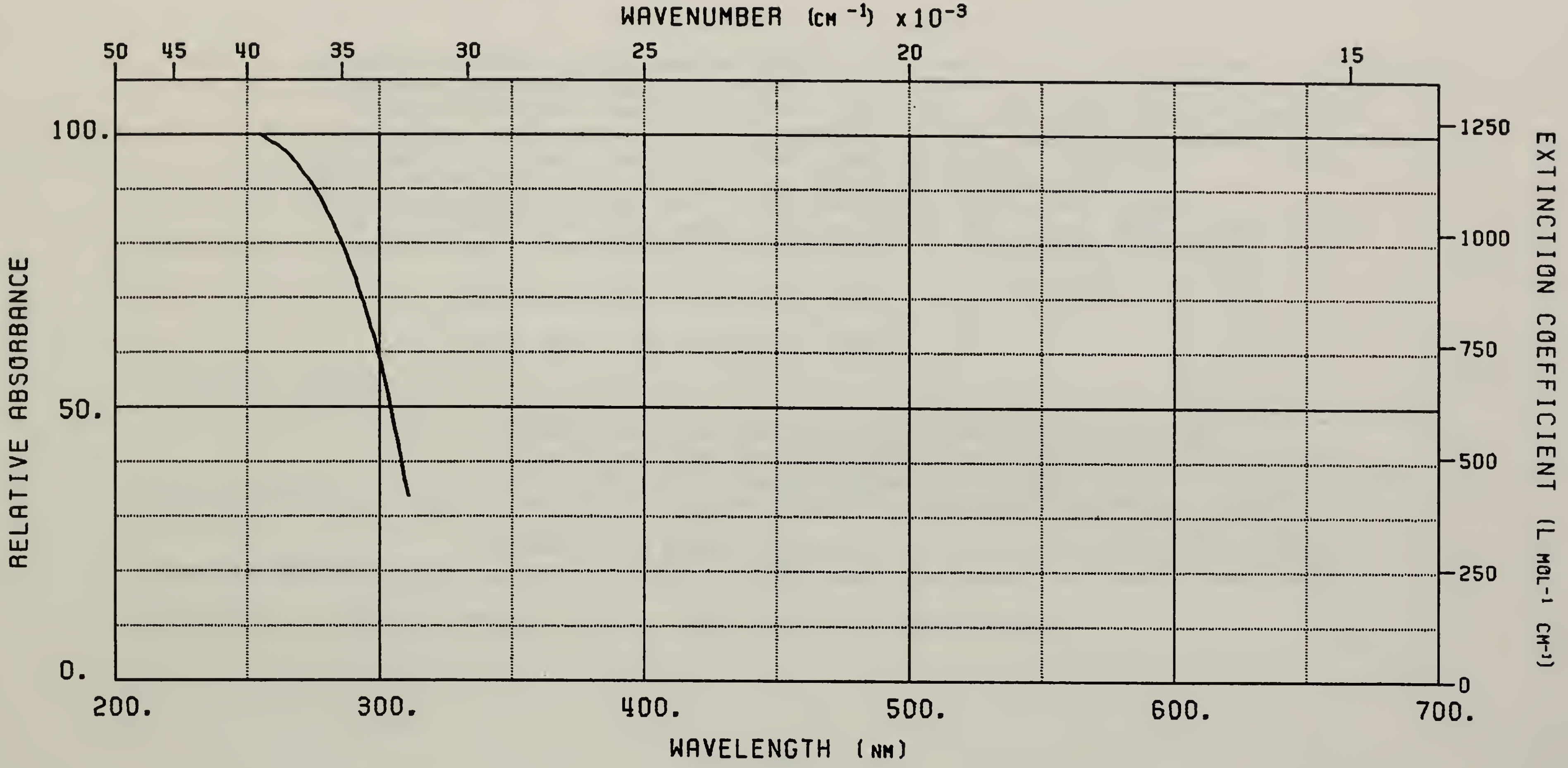
[3] Due to hydrolysis of the salt. Solutions were unbuffered.

[4] L. Dogliotti and E. Hayon, J. Phys. Chem. 71: 2511-6 (1967).

[5] Mechanism proposed by T.W. Martin and M.V. Stevens, The 12th Informal Conference on Photochemistry, June 28 - July 1, 1976, Natl. Bur. Stds., Gaithersburg, MD, Extended Abstracts, G2, p.1-5.

[6] Other mechanisms for formation have been proposed, i.e. see reference in footnote [4].

NO^-



Transient: NO^-, λ(max) ≈ 260 nm, ϵ_{260} ≈ 1200 L mol^{-1} cm^{-1} [1,2]

System: aqueous solution of ≈ 10^{-4} mol L^{-1} NO, pH 7.0 (buffered) [3]

NO^-

Reference: W.A. Seddon, J.W. Fletcher, and F.C. Sopchyshyn, Can. J. Chem. 51(7): 1123-30 (1973)

Transient generation: pulse radiolysis, using Van de Graaff generator; energy 2.25 MeV; pulse length 1 μs; dose per pulse ≈ 3 krad; dosimetry [4]

Spectral acquisition: monitoring lamp [5]; Bausch & Lomb f/3.5 high intensity monochromator; RCA 1P28 or HTV R166 PMT [6]; Tektronix 556 oscilloscope; time delay-immediately after pulse

Transient formation [7]:

$$e(aq)^- + NO \rightarrow NO^-$$

$$H + NO \rightarrow HNO$$

$$HNO \rightleftharpoons NO^- + H^+, \; pK_a(HNO) = 4.7$$

Footnotes:

[1] Extinction coefficient based on $G(NO^-) = G(e(aq)^-) + G(H) = 3.2$.

[2] Earlier value - 1400 L mol^{-1} cm^{-1}, M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges Physik. Chem. 74(10): 1003-10 (1970).

[3] Fresh solutions were used for each pulse.

[4] Using aerated, 2×10^{-3} mol L^{-1} SCN^- solutions and taking $G\epsilon = 2.10 \times 10^4$ for $(SCN)_2^-$ at 475 nm. Relative dose monitored by integrating current striking an Al block.

[5] Either a Hanovia 300 W high pressure xenon lamp operated in DC or pulsed mode, a GE 62 W quartz-iodine lamp, or a 30/50 W deuterium lamp was used.

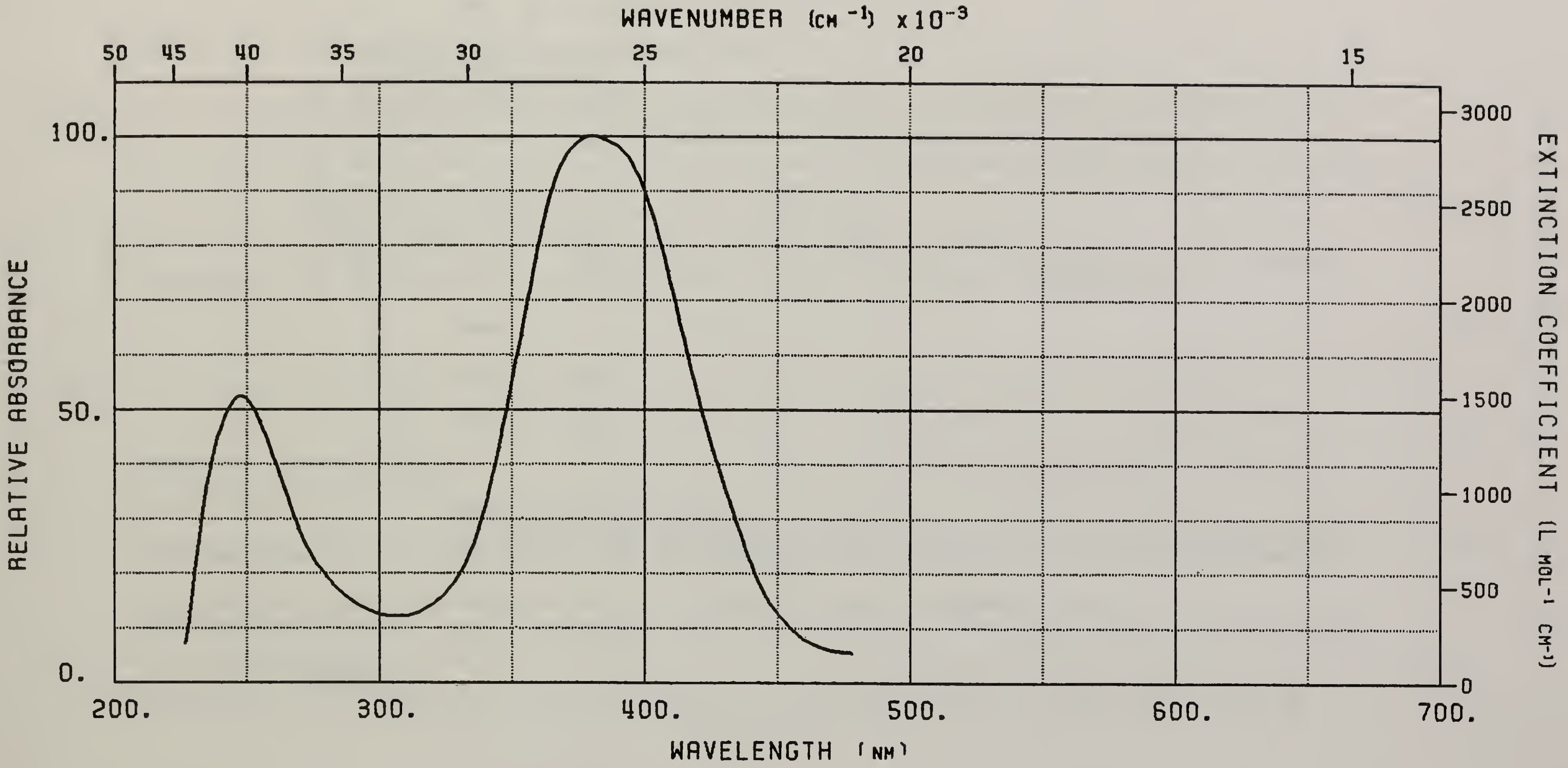
[6] For wavelengths shorter than 300 nm the R166 PMT was used with narrow band pass interference filters.

[7] Hydroxyl radical reactions were

$$OH + NO \rightarrow HNO_2$$

$$HNO_2 \rightleftharpoons H^+ + NO_2^-, \; pK_a(HNO_2) = 3.5$$

$N_2O_2^-$



Transient: $N_2O_2^-$, λ(max) = 380 nm, ε_{380} = (2850 ± 200) L mol^{-1} cm^{-1} [1,2]

System: aqueous solution of ≈ 2 x 10^{-3} mol L^{-1} NO, pH 7.0 (buffered) [3]

$N_2O_2^-$

Reference: W.A. Seddon, J.W. Fletcher, and F.C Sopchyshyn, Can. J. Chem. 51(7): 1123-30 (1973)

Transient generation: pulse radiolysis, using Van de Graaff generator; energy 2.25 MeV; pulse length 1 μs; dose per pulse ≈ 3 krad; dosimetry [4]

Spectral acquisition: monitoring lamp [5]; Bausch & Lomb f/3.5 high intensity monochromator; RCA 1P28 or HTV R166 PMT [6]; Tektronix 556 oscilloscope; time-delay- immediately after pulse

Transient formation [7]:

$$e(aq)^- + NO \rightarrow NO^-$$

$$H + NO \rightarrow HNO$$

$$HNO \rightleftharpoons NO^- + H^+, \ pK_a(HNO) = 4.7$$

$$NO + NO^- \rightleftharpoons N_2O_2^-, \ pK_a(HN_2O_2) = 3.5$$

Footnotes:

[1] Extinction coefficient based on $G(N_2O_2^-) = G(e(aq)^-) + G(H) = 3.2$.

[2] Earlier value - 3300 L mol^{-1} cm^{-1}, M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges Physik. Chem. 74(10): 1003-10 (1970).

[3] Fresh solutions were used for each pulse.

[4] Using aerated, 2×10^{-3} mol L^{-1} SCN$^-$ solutions and taking $G\epsilon = 2.10 \times 10^4$ for $(SCN)_2^-$ at 475 nm. Relative dose monitored by integrating current striking on Al block.

[5] Either a Hanovia 300 W high pressure xenon lamp operated in DC or pulsed mode, a GE 62 W quartz-iodine lamp, or a 30/50 W deuterium lamp was used.

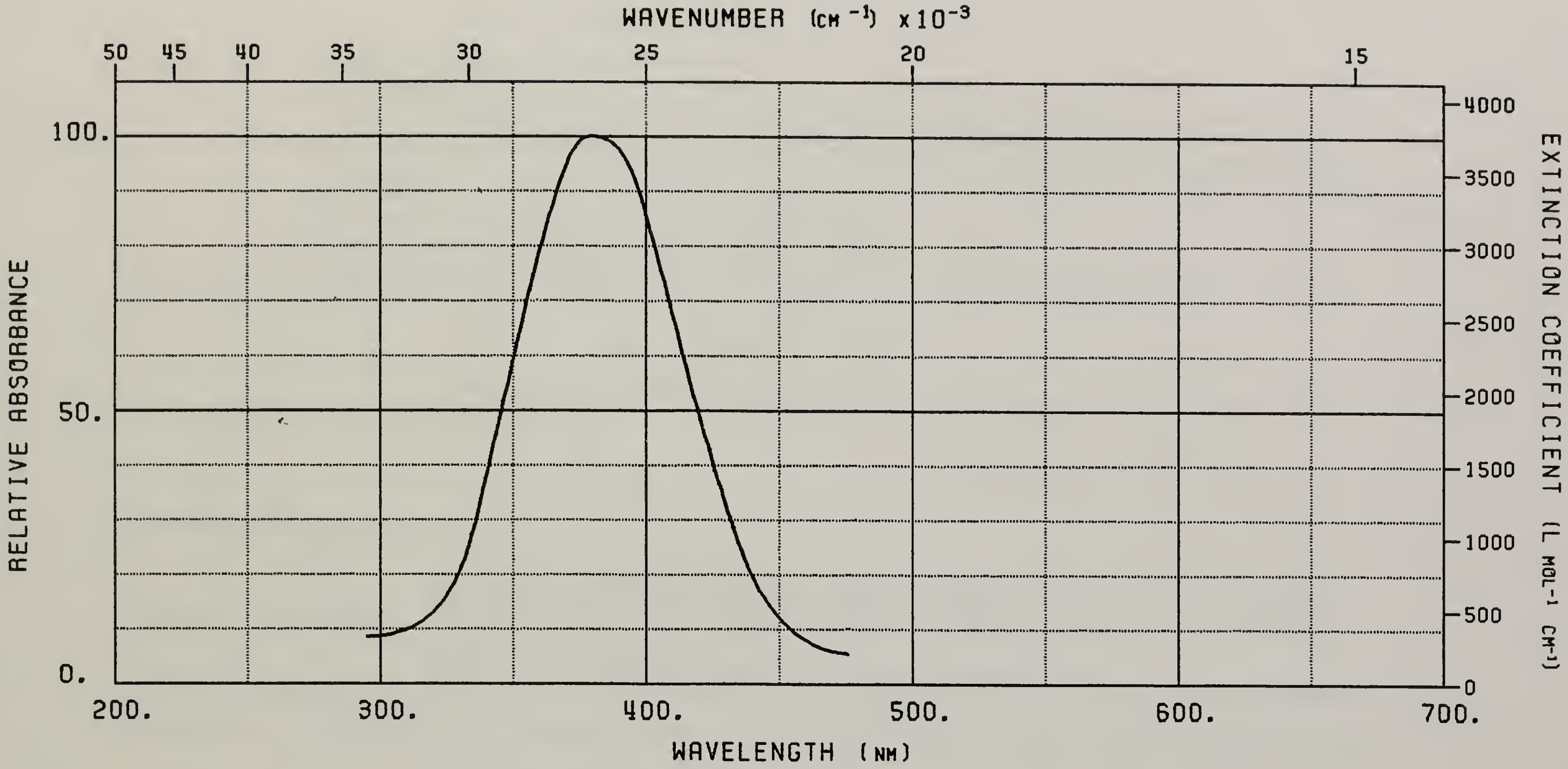
[6] For wavelengths shorter than 300 nm the R166 PMT was used with narrow band pass interference filters.

[7] Hydroxyl radical reactions were

$$OH + NO \rightarrow HNO_2$$

$$HNO_2 \rightleftharpoons H^+ + NO_2^-, \ pK_a(HNO_2) = 3.5$$

$N_3O_3^-$



Transient: $N_3O_3^-$, λ(max) = 380 nm, ϵ_{380} = (3750 ± 300) L mol^{-1} cm^{-1} [1,2]

System: aqueous solution of ≈ 2 x 10^{-3} mol L^{-1} NO, pH 7.0 (buffered) [3]

$N_3O_3^-$

Reference: W.A. Seddon, J.W. Fletcher, and F.C. Sopchyshyn, Can. J. Chem. 51(7): 1123-30 (1973)

Transient generation: pulse radiolysis, using Van de Graaff generator; energy 2.25 MeV; pulse length 1 μs; dose per pulse ≈ 3 krad; dosimetry [4]

Spectral acquisition: monitoring lamp [5]; Bausch 8 Lomb f/3.5 high intensity monochromator; RCA 1P28 or HTV R166 PMT [6]; Tektronix 556 oscilloscope; time delay-extrapolated back to end of pulse

Transient formation [7]:

$e(aq)^- + NO \rightarrow NO^-$

$H + NO \rightarrow HNO$

$HNO \rightleftharpoons NO^- + H^+$, $pK_a(HNO) = 4.7$

$NO^- + NO \rightleftharpoons N_2O_2^-$, $pK_a(HN_2O_2) = 3.5$

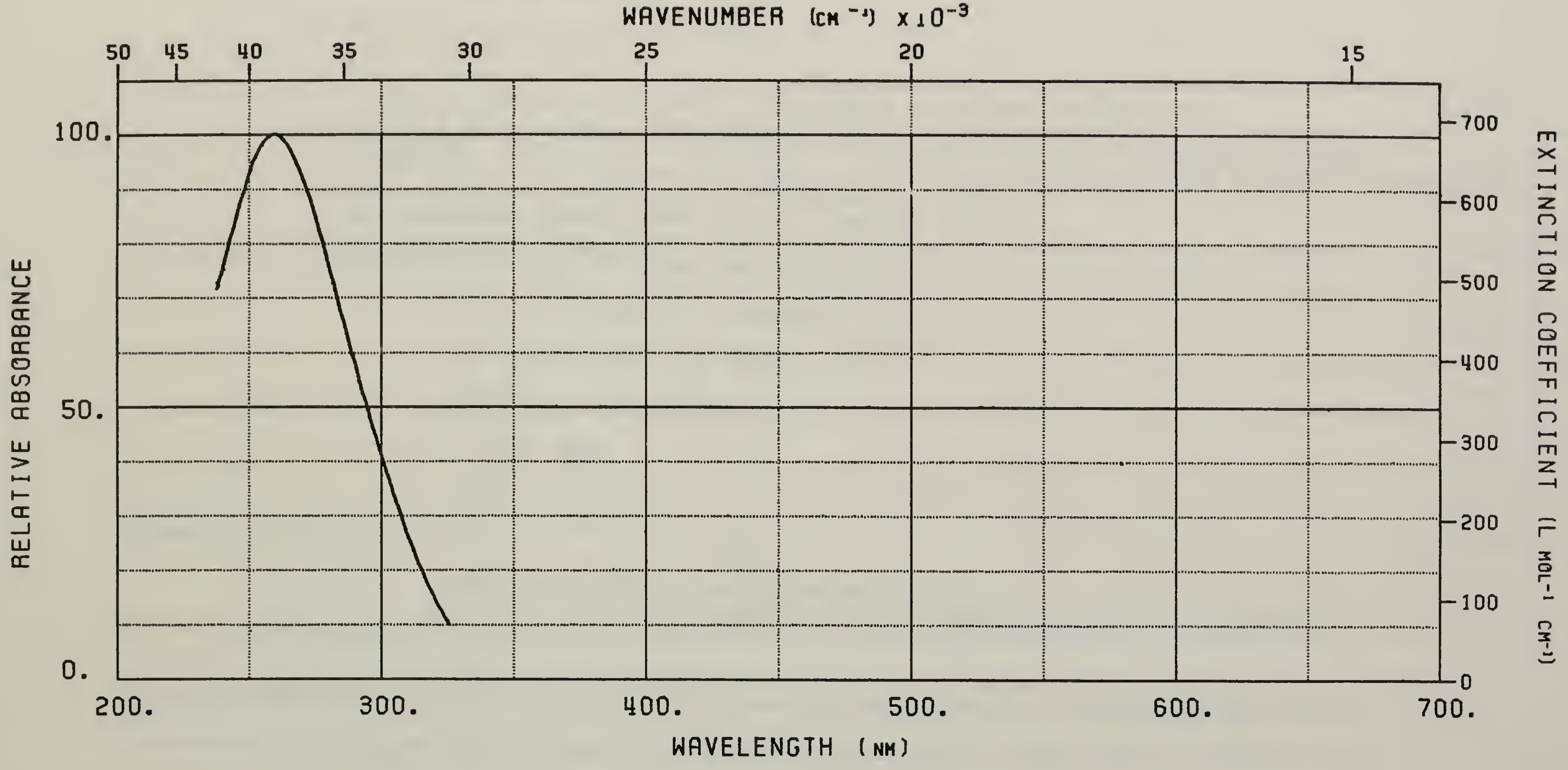
$N_2O_2^- + NO \rightleftharpoons N_3O_3^-$, $pK_a(HN_3O_3) = 3.1$

Footnotes:
[1] Extinction coefficient based on $G(N_3O_3^-) = G(e(aq)^-) + G(H) = 3.2$.
[2] Earlier value - 4000 L mol^{-1} cm^{-1}, M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges Physik. Chem. 74(10): 1003-10 (1970).
[3] Fresh solutions were used for each pulse.
[4] Using aerated, 2×10^{-3} mol L^{-1} SCN^- solutions and taking $G\epsilon = 2.10 \times 10^4$ for $(SCN)_2^-$ at 475 nm. Relative dose monitored by integrating current striking an Al block.
[5] Either a Hanovia 300 W high pressure xenon lamp operated in DC or pulsed mode, a GE 62 W quartz-iodine lamp, or a 30/50 W deuterium lamp was used.
[6] For wavelengths shorter than 300 nm the R166 PMT was used with narrow band pass interference filters.
[7] Hydroxyl radical reactions were

$OH + NO \rightarrow HNO_2$

$HNO_2 \rightleftharpoons H^+ + NO_2^-$, $pK_a(HNO_2) = 3.5$

NO_2^{2-}



Transient: NO_2^{2-} [1], λ(max) = 260 nm, ϵ_{260} = 680 L mol^{-1} cm^{-1}

System: aqueous solution of 2.5 x 10^{-4} mol L^{-1} NO_2^- and 0.25 mol L^{-1} tert-butanol, pH = 9, Ar-saturated

NO_2^{2-}

Reference: M. Graetzel, A. Henglein, J. Lilie, and G. Beck, Ber. Bunsenges. Physik. Chem. 73(7): 646-53 (1969)

Transient generation: pulse radiolysis [2] using Van de Graaff generator; energy 1.6 MeV

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

Transient formation:

$$OH + (CH_3)_3COH \rightarrow H_2O + CH_2C(CH_3)_2OH$$

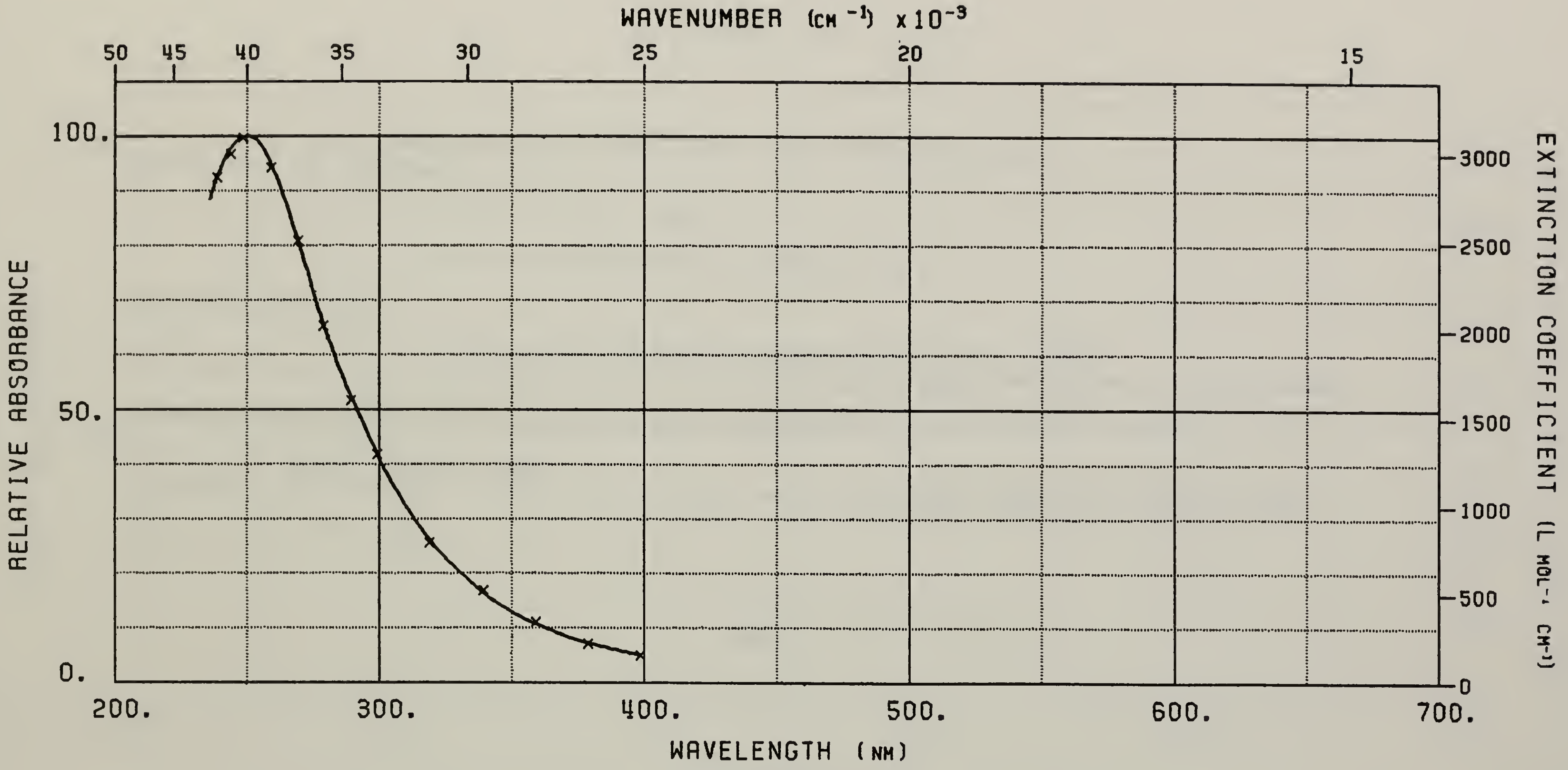
$$NO_2^- + e(aq)^- \rightarrow NO_2^{2-}$$

Footnotes:

[1] $pK_a(HNO_2^-) = 7.7$.

[2] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

NO_3^{2-}



Transient: NO_3^{2-}, λ(max) = 250 nm, ϵ_{250} = 3100 L mol^{-1} cm^{-1} [1]

System: aqueous solution of 2 x 10^{-4} mol L^{-1} NO_3^- and 0.1 mol L^{-1} tert-butanol, pH 9.5

$NO_3{}^{2-}$

Reference: M. Graetzel, A. Henglein, and S. Taniguchi, Ber. Bunsenges. Physik. Chem. 74(3): 292-8 (1970)

Transient generation: pulse radiolysis [2], using Van de Graaff generator

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay, immediately after pulse

Transient formation:

$$OH + (CH_3)_3COH \rightarrow H_2O + CH_2C(CH_3)_2OH$$

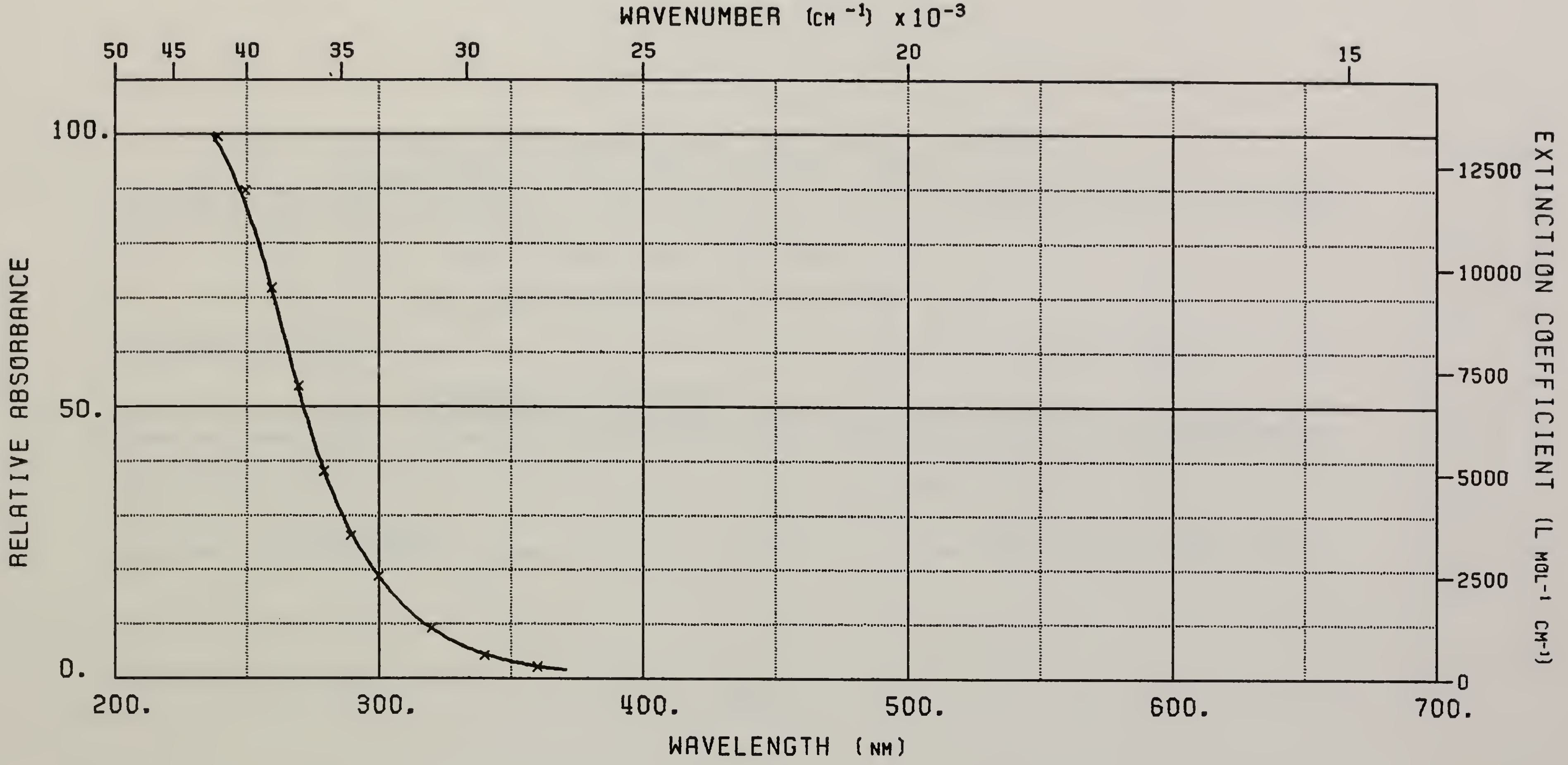
$$e(aq)^- + NO_3{}^- \rightarrow NO_3{}^{2-},\ pK_a(HNO_3{}^-) = 7.5$$

Footnotes:

[1] Based on $G(e(aq)^-) = 2.7$. Effect of H atom was neglected because rate constant for reaction of H with $NO_3{}^-$ is small, $k = 3.8 \times 10^6$ L mol^{-1} s^{-1} from G. Navon and G. Stein, J. Phys. Chem. 69: 1384-9 (1965).

[2] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

N_2O_3



Transient: N_2O_3 [1,2]

System: aqueous solution of 2.0×10^{-5} to 1.04×10^{-4} mol L^{-1} NO, 2×10^{-4} to 3×10^{-4} mol L^{-1} NO_2^-, and 2.4×10^{-2} mol L^{-1} N_2O

N_2O_3

Reference: M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges. Physik. Chem. 74(5): 488-92 (1970)

Transient generation: pulse radiolysis [3], using Van de Graaff generator; energy 1.5 MeV; dose rate during the pulse was 700 rad per μs

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 20 μs

Transient formation [4]:

$$N_2O + e(aq)^- \; (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$NO_2^- + OH \rightarrow NO_2 + OH^-$$

$$NO_2 + NO \rightleftharpoons N_2O_3, \; K = 1.4 \times 10^4 \text{ L mol}^{-1}$$

Footnotes:

[1] Extinction coefficient was obtained by assuming that the yield of $NO_2 + N_2O_3$ was equal to the initial yield of NO_2.

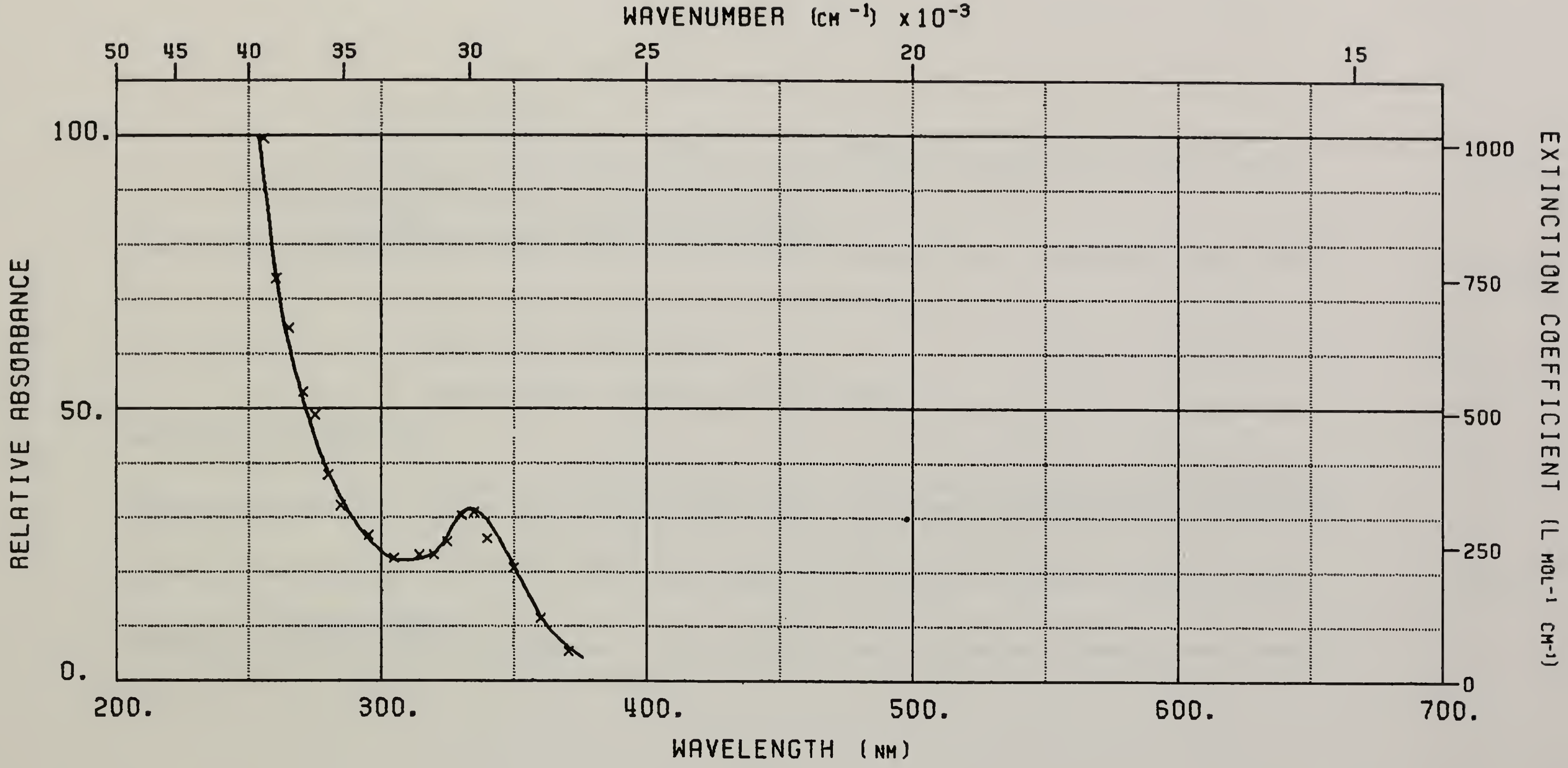
[2] Spectrum corrected for NO_2 absorption.

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[4] Reaction of OH with NO does not involve complications since little reacts under the experimental conditions. Any NO that does react with OH only reforms the initial reactants

$$NO + OH \rightarrow NO_2^- + H^+$$

N_2O_4



Transient [1]: N_2O_4, $\lambda(\max) \approx 340$ nm, $\epsilon_{335} = (320 \pm 60)$ L mol^{-1} cm^{-1} [2]

System: aqueous solution of 9.5×10^{-4} mol L^{-1} NO_2^-, saturated with N_2O ($\approx 2.5 \times 10^{-2}$ mol L^{-1}), pH 5.0

N_2O_4

Reference: A. Treinin and E. Hayon, J. Am. Chem. Soc. 92(20): 5821-8 (1970)

Transient generation [3]: pulse radiolysis, using Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length ~ 30 ns; dosimetry using N_2O-saturated aqueous solution of 0.1 KSCN [4]

Spectral acquisition [3]: Osram XBO 450 W xenon lamp (pulsed); two high-intensity Bausch & Lomb monochromators, used in series to reduce scattered light [5]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscillosocope; time delay 160 μs after pulse

Transient formation:

$$N_2O + e(aq)^- \ (+H_2O) \rightarrow OH + OH^- + N_2$$

$$OH + NO_2^- \rightarrow NO_2 + OH^-$$

$$2NO_2 \rightleftharpoons N_2O_4, \ K^{-1} = (1.3 \pm 0.4) \times 10^{-5} \text{ mol L}^{-1}$$

Footnotes:

[1] Absorption at wavelength shorter than 300 nm may be partially due to N_2O_3 which can be formed by

$$NO + NO_2 \rightarrow N_2O_3$$

where NO was produced by H atom reactions.

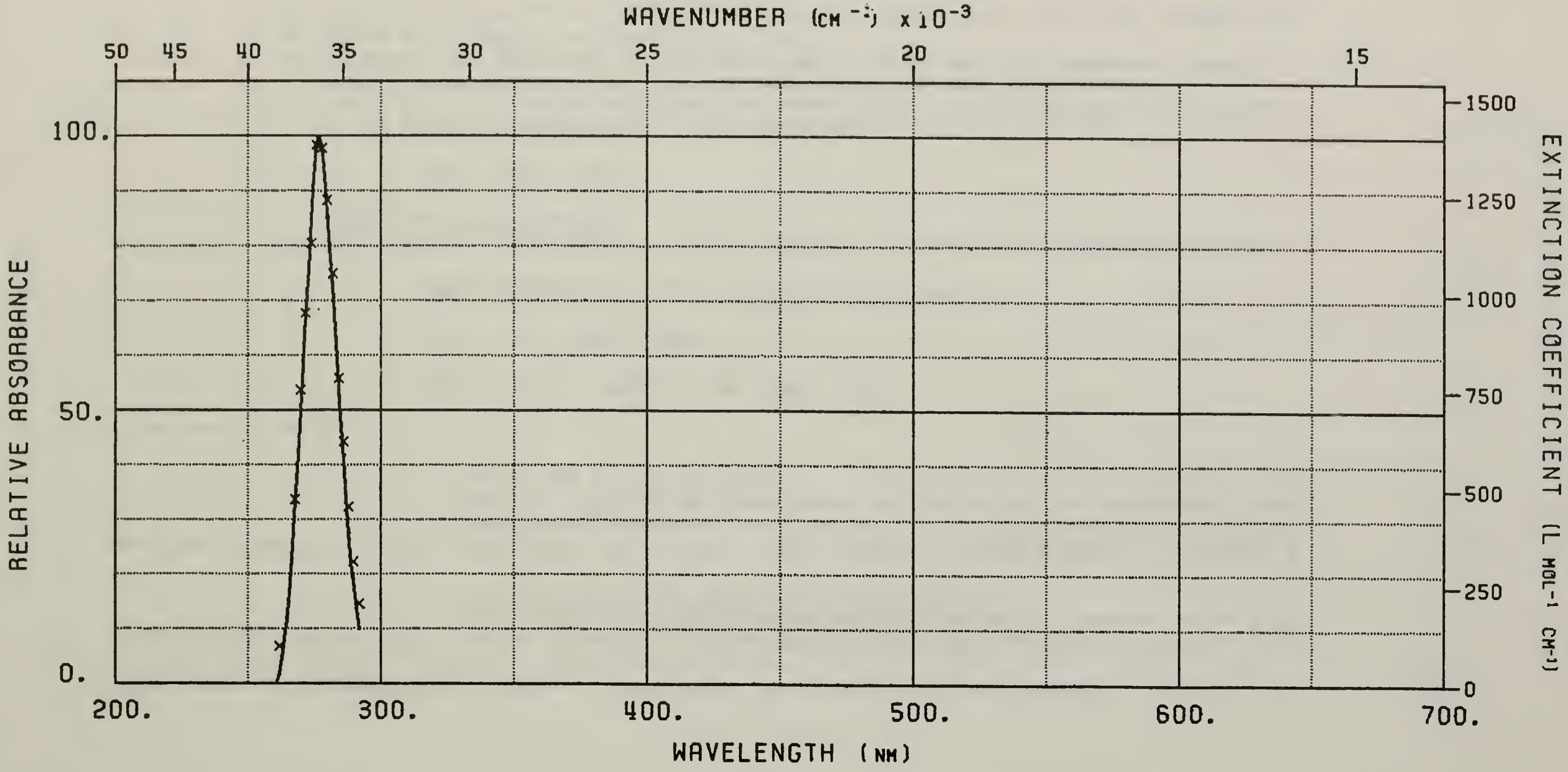
[2] Based on equilibrium equations for equilibrium of NO_2 and N_2O_4 and taking $\epsilon(NO_2) = 200$ L mol^{-1} cm^{-1} at the maximum of the NO_2 spectrum.

[3] M. Simic, P. Neta, and E. Hayon, J. Phys. Chem. 73(11): 3794-800 (1969).

[4] Using ϵ_{500} $(SCN)_2^-$ = 7600 L mol^{-1} cm^{-1}.

[5] At 230 and 210 nm the amount of scattered light was 1% and 18%, respectively.

N_3



Transient [1]: N_3, azide radical, λ(max) = 277 nm, ϵ_{275} = 1400 L mol^{-1} cm^{-1} [2,3], 2k = (8.0 ± 0.7) x 10^9 L mol^{-1} s^{-1} [2]

System: aqueous solution of 10^{-4} mol L^{-1} NaN_3, pH ~ 9.4, N_2-saturated

N_3

Reference: A. Treinin and E. Hayon, J. Chem. Phys. 50: 538-9 (1969)

Transient generation [4]: flash photolysis with four oxygen flash lamps; total flash energy 1800 J; duration at "1/e" time 5 μs, total flash duration 70 μs

Spectral acquisition [4]: xenon Osram XBO 450 W monitoring lamp; Bausch & Lomb grating monochromator; PMT; Tektronix 535A oscilloscope; spectrum was obtained by a point-by-point method; time delay 120 μs after start of flash

Transient formation:

$$N_3^- + h\nu \rightarrow N_3 + e(aq)^-$$

Footnotes:

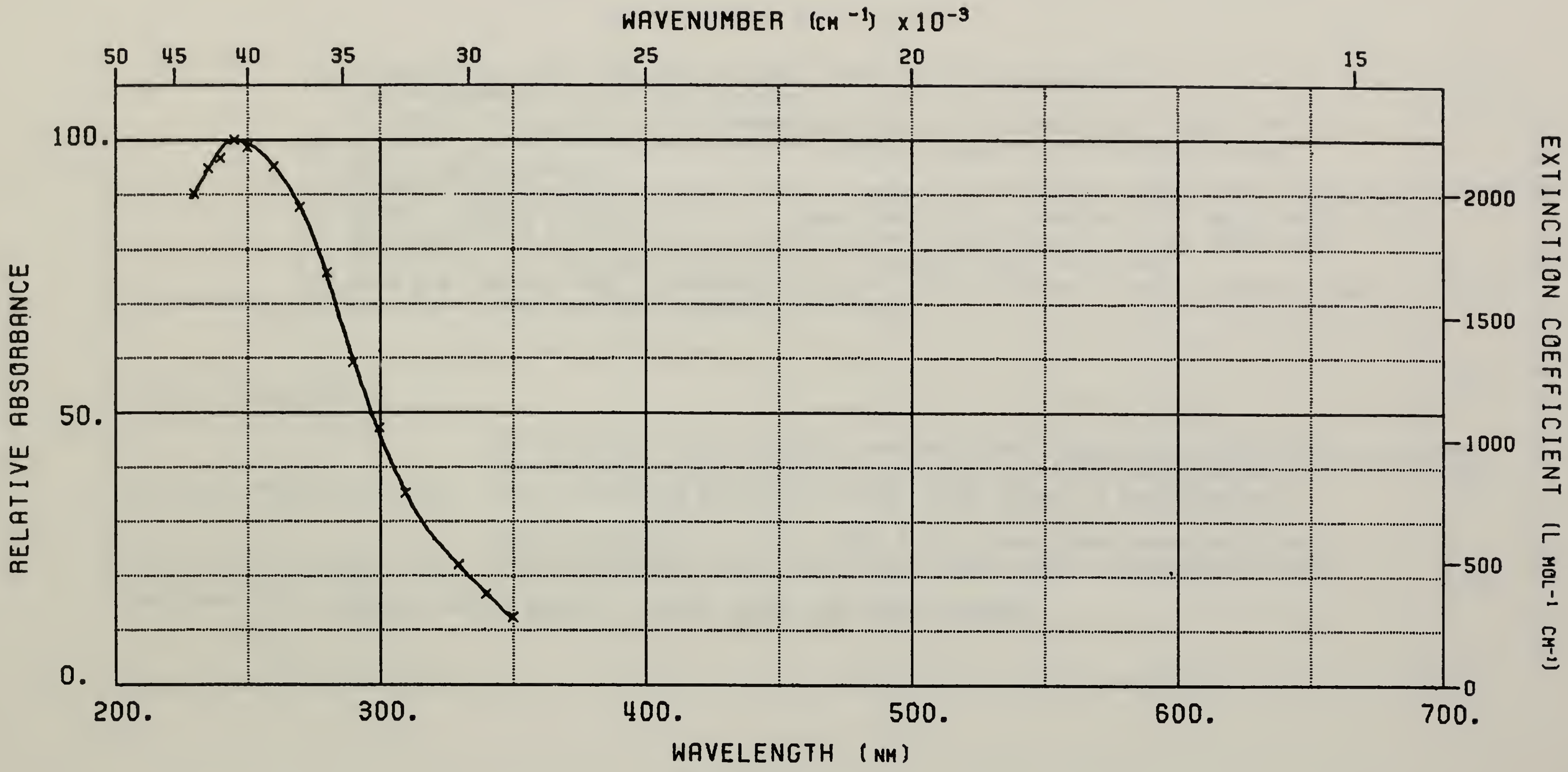
[1] Each data point was the average of six runs.

[2] From G.V. Buxton and I. Janovsky, J. Chem. Soc., Faraday 1 72(8): 1884-6 (1976). Other sets of ϵ and 2k for N_3 are ϵ_{278} = 2300 L mol^{-1} cm^{-1} and 2k = (9 ± 1) x 10^9 L mol^{-1} s^{-1} from E. Hayon and M. Simic, J. Am. Chem. Soc. 92(25): 7486-7 (1970); and ϵ_{275} = 1300 L mol^{-1} cm^{-1} and 2k = 6 x 10^9 L mol^{-1} s^{-1} from E.J. Land and W.A. Prutz, Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med. 36(1): 75-83 (1979).

[3] Although the displayed spectrum has $\lambda(max)$ = 277 nm, the $\epsilon(max)$ is shown as 1400 L mol^{-1} cm^{-1} on the assumption that all the authors in this case were making measurements at the maximum.

[4] L. Dogliotti and E. Hayon, J. Phys. Chem. 71(8): 2511-6 (1967).

$\cdot CONH^-$



Transient: $\cdot CONH^-$, $\lambda(max)$ = 245 nm, ϵ_{245} = 2200 L mol^{-1} cm^{-1} [1], 2k = 2.2 x 10^9 L mol^{-1} s^{-1}

System: aqueous solution of 10^{-3} mol L^{-1} CN^- in 1 mol L^{-1} KOH, saturated with N_2O

$\cdot CONH^-$

Reference: D. Behar, J. Phys. Chem. 78(26): 2660-3 (1974)

Transient generation: pulse radiolysis, using electrons from Van de Graaff generator; energy 2.8 MeV; pulse length 0.5-2 μs; dose 1-5 krad [2]

Spectral acquisition [3]: single-pass cell, pulsed Osram 450 W XBO xenon monitoring lamp; Bausch 8 Lomb monochromator, focal length 500 cm, bandwidth 2 nm; EMI 9558 QC PMT; corrected for stray light below 240 nm

Transient formation [4]:

$OH^- + OH \rightarrow O^- + H_2O$, $pK_a(OH) = 11.85$

$O^- + CN^- \rightarrow {}^-O\text{-}C{=}N^-$

${}^-O\text{-}C{=}N^- + H_2O \rightarrow {}^-O\text{-}C{=}NH + OH^-$

${}^-O\text{-}C{=}NH \rightarrow O{=}C\text{-}NH^-$, $pK_a(NH_2C{=}O) = 12.25$

Footnotes:

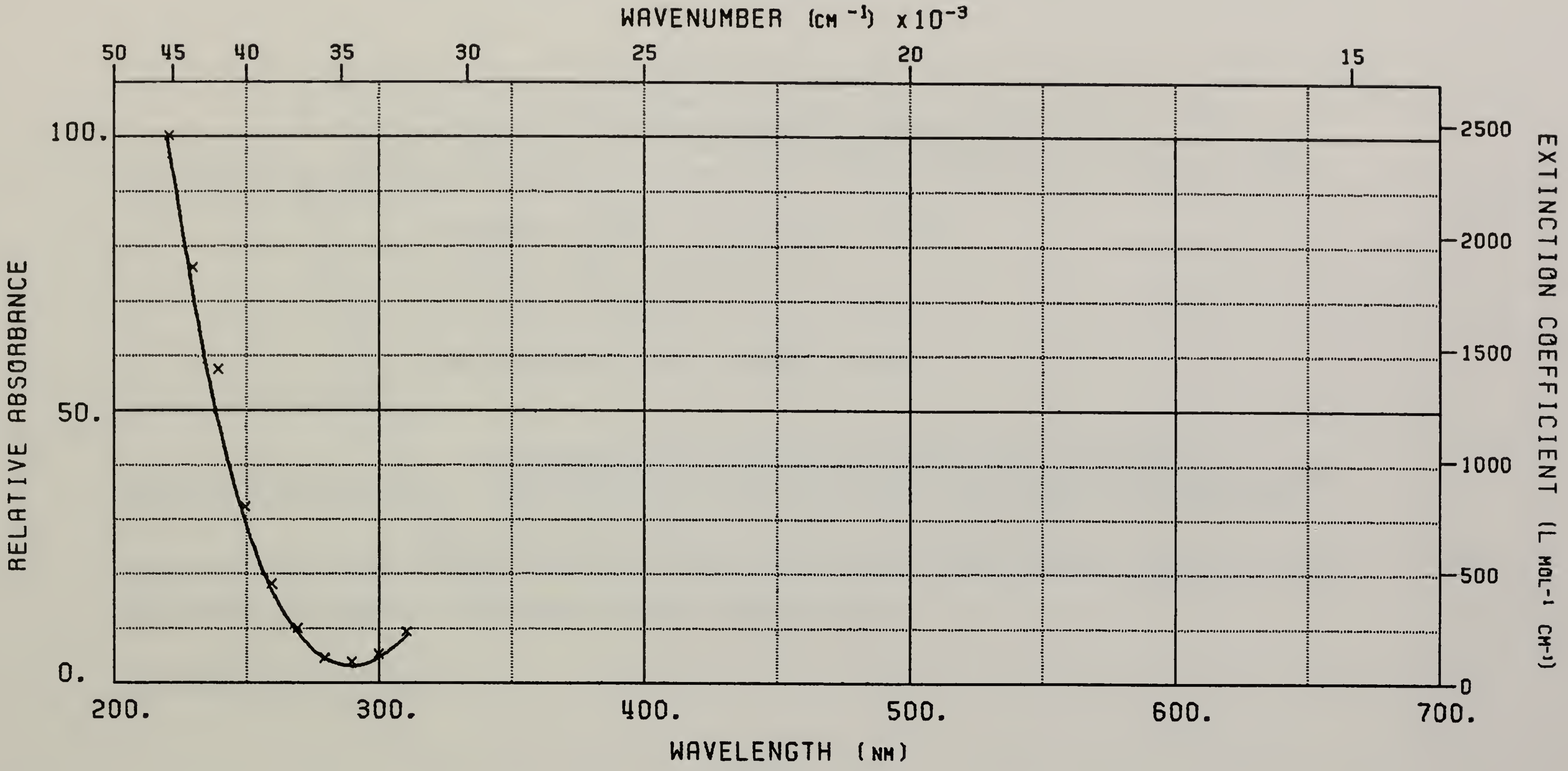
[1] Extinction coefficient determined by comparing absorption to $(SCN)_2^-$ with $\epsilon(max) = 7600\ L\ mol^{-1}\ cm^{-1}$ and by assuming G(radicals) = $G(e(aq)^-) + G(OH)$.

[2] Electron beam monitored by a secondary emission monitor.

[3] L.K. Patterson and K.M. Bansal, J. Phys. Chem. 76(17): 2392-9 (1972).

[4] H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976).

$O{=}CNH_2$



Transient: $O{=}CNH_2$ [1,2], $2k = 6.2 \times 10^9$ L mol^{-1} s^{-1}

System: variety of aqueous solutions of either 10^{-1} mol L^{-1} CN^- or 10^{-2} mol L^{-1} CN^-, pH 9.85 to 11.5; all solutions saturated with N_2O

$O{=}CNH_2$

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [3]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose 25.8 to 31.2 krad

Spectral acquisition [3]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556)

Transient formation:

$$e(aq)^- + N_2O(+H_2O) \rightarrow N_2 + OH + OH^-$$

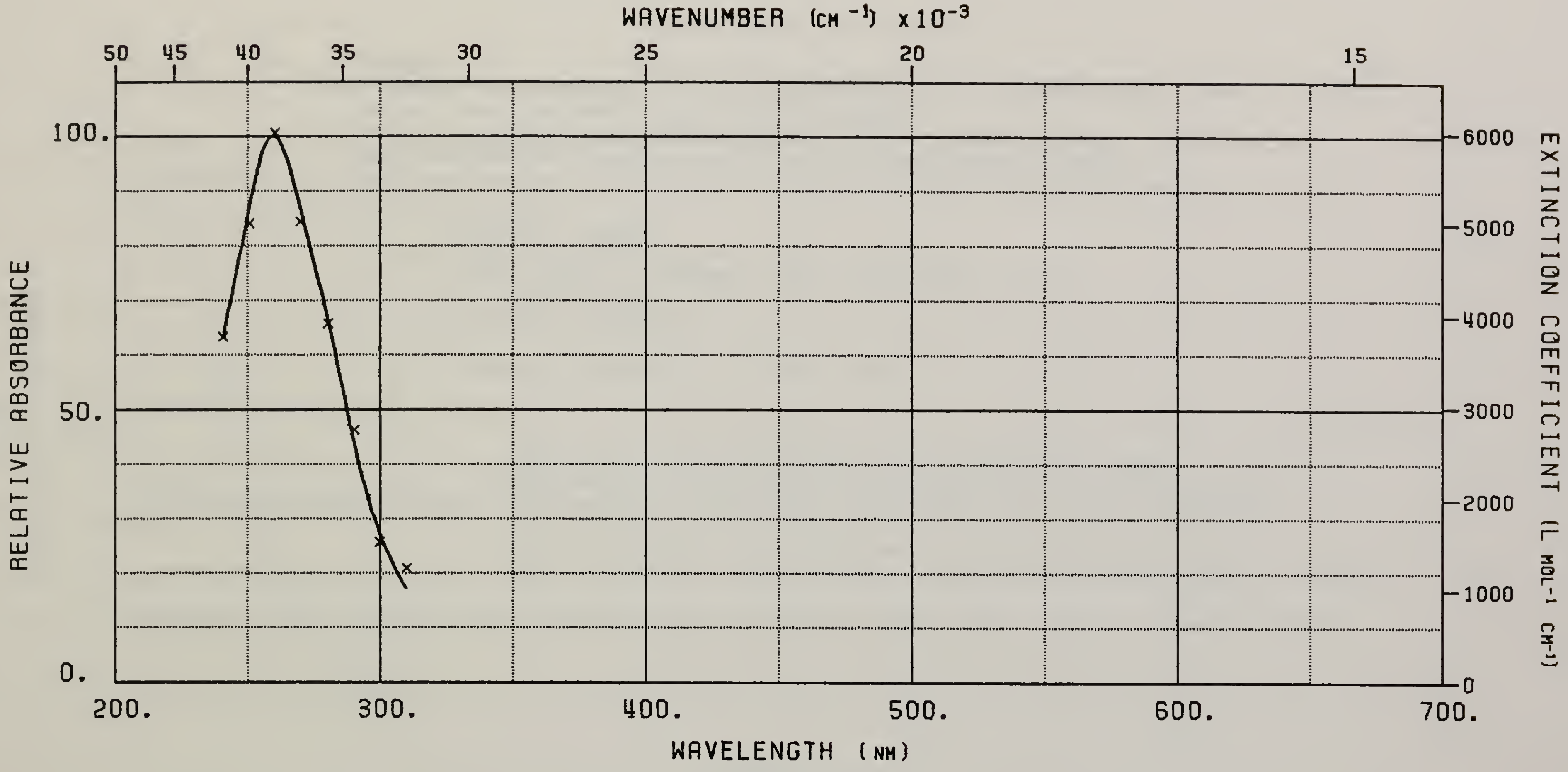
$$OH + CN^- \rightarrow HOC{=}N^-$$

$$H_2O + HOC{=}N^- \rightleftharpoons HOC{=}NH + OH^-,\ pK_a(HOC{=}NH) = 10.2$$

$$HOC{=}NH \rightarrow O{=}CNH_2$$

Footnotes:
[1] Spectrum corrected for spectra of the precursors $HOC{=}NH$ and $HOC{=}N^-$. This was done by computer simulation of the kinetic scheme.
[2] Earlier spectrum by D. Behar, J. Phys. Chem. 78(26): 2660-3 (1974), shows a weak maximum in the region of 320 nm.
[3] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

HOC=NH



Transient: HOC=NH [1]

System [2]: aqueous solution of 10^{-2} mol L^{-1} CN^{-}, pH 9.85, saturated with N_2O

HOC=NH

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [3]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 25.8 krad

Spectral acquisition [3]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556); time delay variable [4]

Transient formation:

$$e(aq)^- + N_2O(+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + CN^- \rightarrow HOC{=}N^-$$

$$H_2O + HOC{=}N^- \rightleftharpoons HOC{=}NH + OH^-, \ pK_a(HOC{=}NH) = 10.2$$

Footnotes:

[1] Spectrum was obtained from a computer simulation using the above equations in addition to known rate constants and

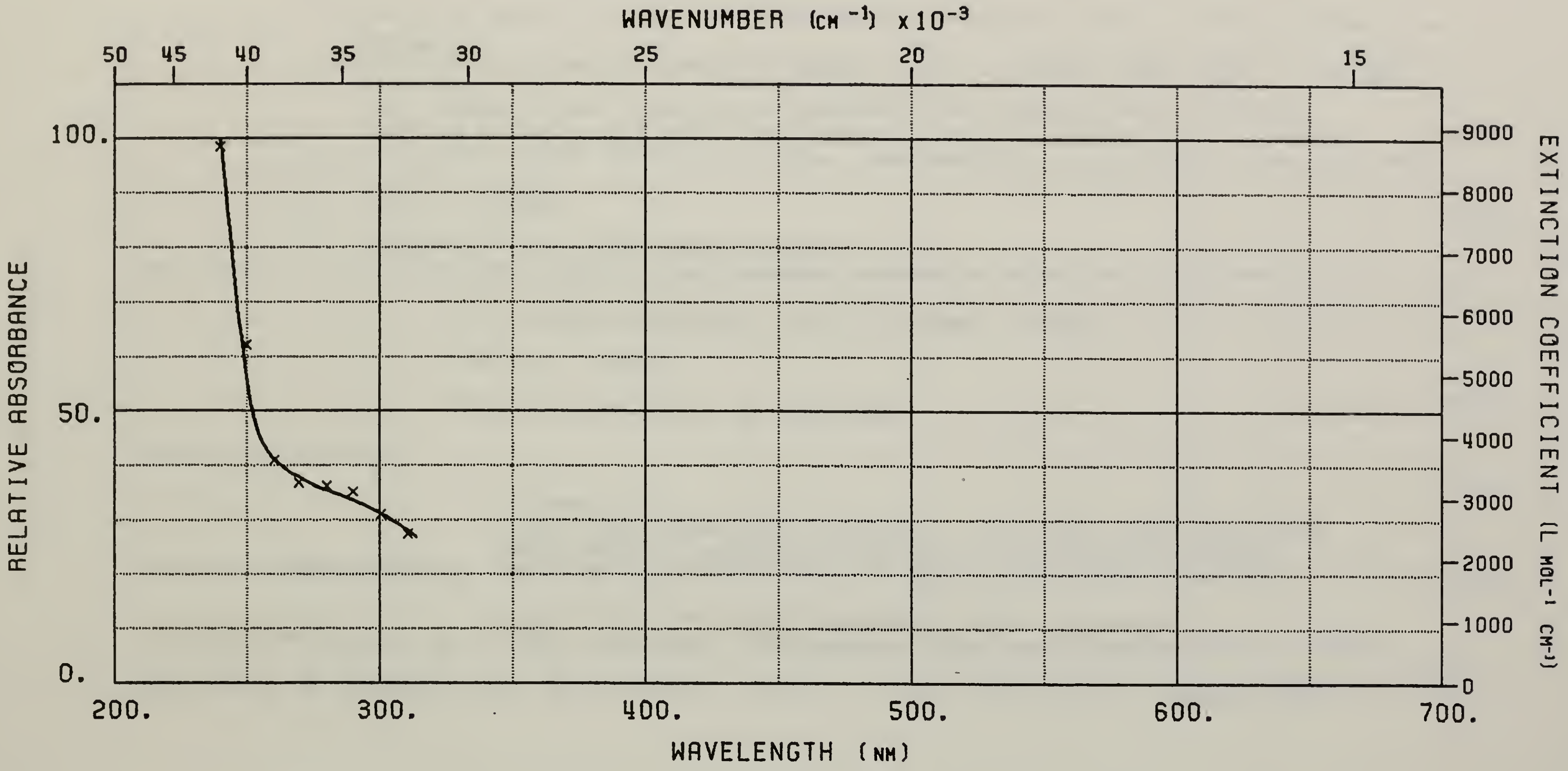
$$HOC{=}NH \rightarrow O{=}CNH_2.$$

[2] Two other chemical systems were used. One had $[CN^-] = 10^{-2}$ mol L^{-1}, pH 10.7, and received a dose = 25.8 krad. The other had $[CN^-] = 10^{-1}$ mol L^{-1}, pH = 11.4, and received a dose = 28.1 krad. Both of these solutions were saturated with N_2O.

[3] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

[4] Transient makes contribution to experimental spectrum only for time less than 1 μs.

$HOC{=}N^-$



Transient: $HOC{=}N^-$ [1]

System [2]: aqueous solution of 10^{-2} mol L^{-1} CN^-, pH 10.7, saturated with N_2O

$HOC{=}N^-$

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [3]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 25.8 krad

Spectral acquisition [3]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556); time delay variable [4]

Transient formation:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + CN^- \rightarrow HOC{=}N^-,\ pK_a(HOC{=}NH) = 10.2$$

Footnotes: [1] Spectrum was obtained from a computer simulation of the

$$OH + CN^- \rightarrow HOC{=}N^-$$

$$H_2O + HOC{=}N^- \rightleftharpoons HOC{=}NH + OH^-$$

$$HOC{=}NH \rightarrow O{=}CNH_2$$

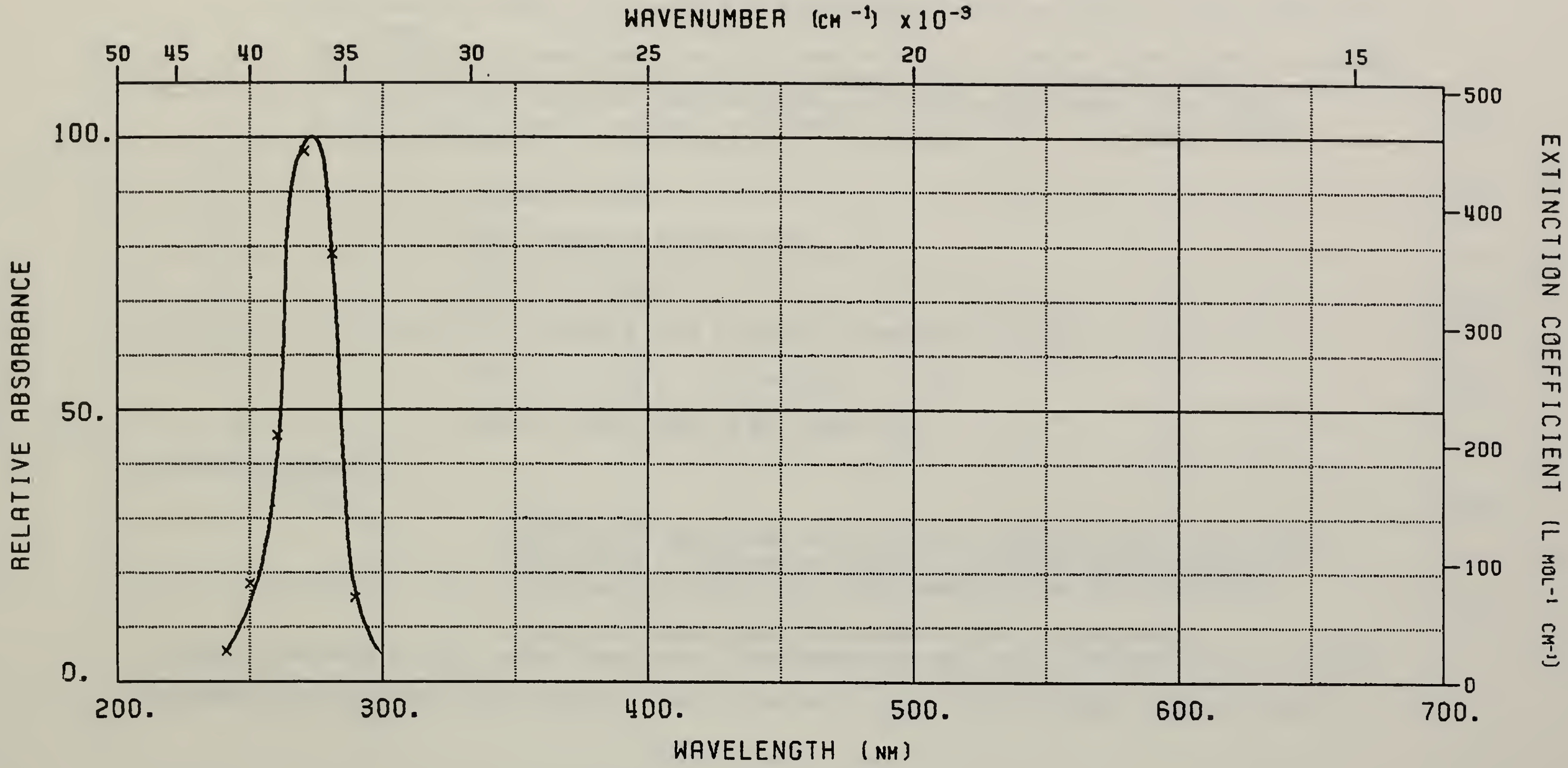
system, using known rate constants.

[2] Two other chemical systems were used at pH 9.85 and 11.4. $[CN^-]$, $[N_2O]$, and the dose were the same in the pH 9.85 system; but $[CN^-] = 10^{-1}$ in the pH 11.4 system, and the dose was 28.1 krad in the pH 11.4 system.

[3] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

[4] Transient makes contribution to experimental spectrum only for time less than 1 μs.

H_2CN



Transient: H_2CN [1], 2k = (2.6 ± 0.8) x 10^9 L mol^{-1} s^{-1}

System: aqueous solution of 10^{-1} mol L^{-1} HCN, pH 1.9

H_2CN

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [2]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 34.8 krad

Spectral acquisition [2]: xenon XBO 450 monitoring lamp; Bausch 8 Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556)

Transient formation:

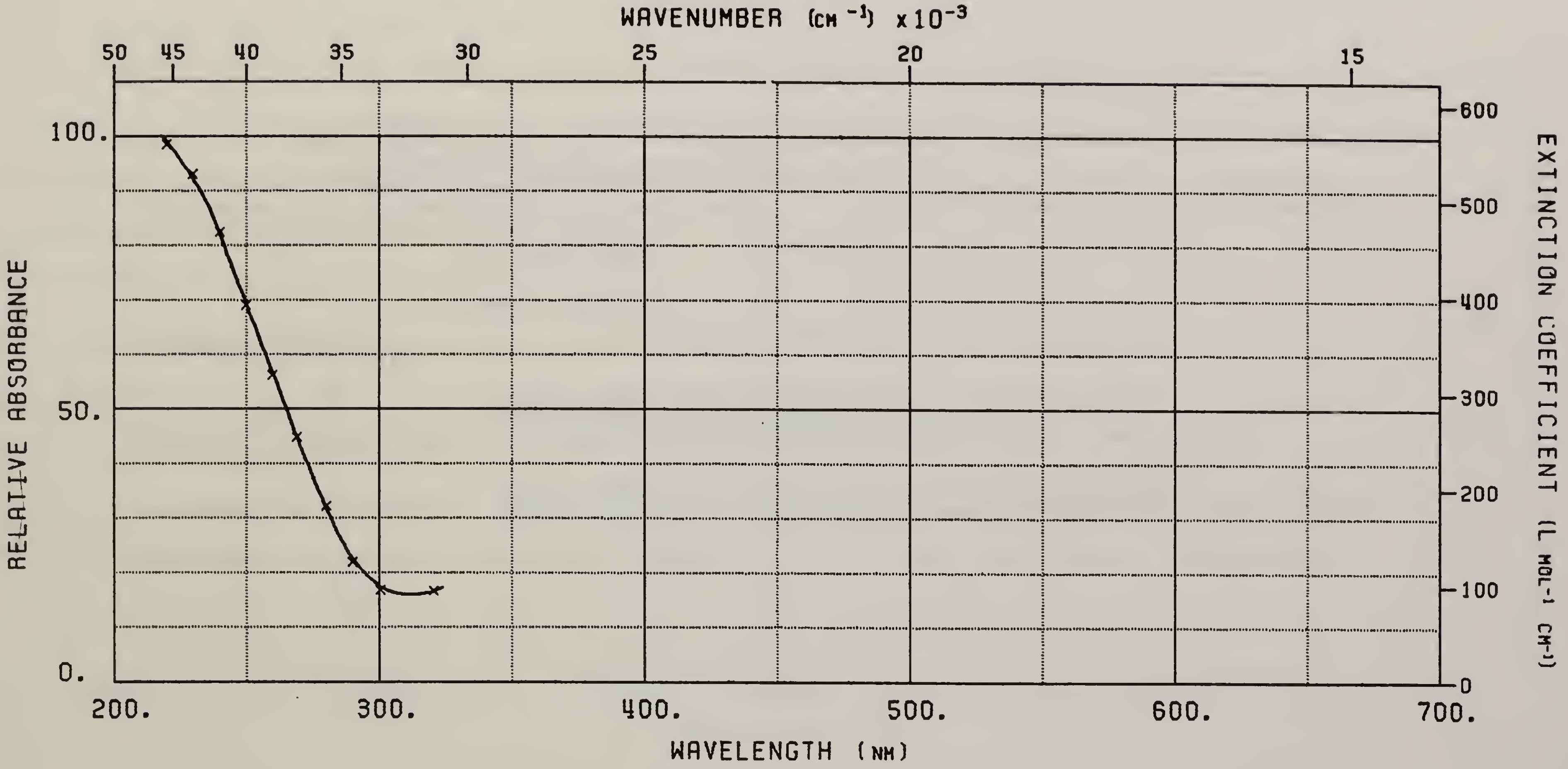
$$e(aq)^- + H^+ \rightarrow H$$

$$H + HCN \rightarrow H_2CN$$

Footnotes: [1] Spectrum determined using computer optimization of some of the rate constants plus computer analysis of spectra from the pH 1.9 HCN system and other acidic HCN solutions which were saturated with N_2O.

[2] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

HOCH=N·



Transient: HOCH=N· [1], $2k = (2.8 \pm 0.5) \times 10^9$ L mol^{-1} s^{-1}

System: aqueous solution of 10^{-1} mol L^{-1} HCN, pH 2.85, saturated with N_2O

HOCH=N·

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [2]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 34.8 krad

Spectral acquisition [2]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556)

Transient formation:

$$e(aq)^- + N_2O\ (+H_2O) \rightarrow N_2 + OH + OH^-$$

$$OH + HCN \rightarrow HOCH{=}N\cdot,\ pK_a(HOCH{=}N\cdot) = 5$$

Footnotes:

[1] Spectrum corrected for OH absorption and the H atom reaction product, H_2CN. This was done using computer simulation.

[2] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

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